

## COMPLETED PROJECT SUMMARY

TITLE : Novel Molecular Sources for Dispersing Boron in Carbon-Carbon Composites

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### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS :

Current boron particle based systems do not provide continuous oxidation protection of inhibited carbon-carbons, especially in the boron-lean carbon matrix neighboring the boron particles. This problem is exacerbated because boron particles cannot be added during impregnation steps due to viscosity limitations. While oxidation inhibiting coatings can improve the oxidation resistance of carbon-carbons, the boron-lean matrix still suffers severe oxidation when the coatings fail. Chemical addition of boron to the matrix-forming resin, on a molecular scale, can improve the oxidation resistance of the impregnated matrices and enable the production of carbon-carbons with superior oxidation resistance and long mission life.

Carborane, a robust molecular source of boron, was chosen as the precursor for atomically dispersed boron. In the Phase I effort, additions of carborane into phenolic resins dramatically improved the oxidation resistance of the carbonized char. The char yield of the phenolic resin was also increased significantly.

A serious drawback of this boron based oxidation inhibition is moisture sensitivity. Protection of the carbon matrix is provided by sacrificial oxidation of the boron, whose high reactivity with oxygen makes it an efficient oxygen scavenger. However, the resulting boron oxide, boria, has a high moisture affinity at ambient conditions. Hydrolysis of the boria and the associated volume expansion, plus release of water vapor at high use temperatures, compromises the structural stability and oxidation

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resistance of the composite. In the Phase II effort, carborane-phenolic chemistry was studied, and modifications of resin systems were used to improve the moisture resistance of the carbon chars.

The Phase II program also characterized the performance of various carbon precursor resins in attempt to minimize boria formation during carbonization, and decrease moisture pick-up. It has been demonstrated that furfuryl based resin systems show reduced premature oxidation of the boron compared to phenolic, and that incorporation of the carborane within a liquid pitch resin blend (Kaiser Code88A) precludes the hydrolysis problem. Code88A reduced oxygen and boria content in the carbonized char and substantially improved its moisture resistance. This moisture resistant resin system was used to densify carbon fiber reinforced carbon-carbon composite panels.

Physical and mechanical properties (such as tensile strength, interlaminar shear strength, and thermal expansion coefficient) of the carborane modified composite were determined and compared with that of baseline materials. No significant difference in the physical and mechanical properties was detected between these two systems. Since oxidation resistance of the carbon chars depends strongly on sample size (or surface area), carborane inhibited carbon-carbon composites performed poorly in the oxidation screening due to size limitation of the matrix carbon. A higher inhibitor concentration helped overcome this problem in the analysis of limited size samples.

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## Summary

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A serious drawback of this boron based oxidation inhibition is moisture sensitivity. Protection of the carbon matrix is provided by sacrificial oxidation of the boron, whose high reactivity with oxygen makes it an efficient oxygen scavenger. However, the resulting boron oxide, boria, has a very high moisture affinity at ambient conditions. Hydrolysis of the boria and the associated volume expansion, plus release of water at high use temperatures, compromises the structural stability and oxidation resistance of the composite. In this Phase II effort, carborane-phenolic chemistry was studied, and modifications of resin systems were used to improve the moisture resistance of the carbon chars.

The Phase II program also characterized the performance of various carbon precursor resins in attempt to minimize boria formation during carbonization and decrease moisture pick-up. It has been demonstrated that furfuryl based resin systems show reduced premature oxidation of the carborane-sourced boron compared to phenolic, and that incorporation of the carborane within a liquid pitch resin blend (Kaiser Code88A) precludes the hydrolysis problem. The use of Code88A resulted in reduced oxygen and boria content in the carbonized char and substantially improved its moisture resistance. This moisture resistant resin system was used to densify carbon fiber reinforced carbon-carbon composite panels. Physical and mechanical properties (such as tensile strength, interlaminar shear strength, and thermal expansion coefficient) were determined and compared with that of baseline materials. Finally, the oxidation resistance of the modified composites, with and without SiC protection coating, was assessed.

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## 1. Introduction

Carbon-carbon composites are attractive materials for use in applications requiring strength, light weight and toughness at high temperatures. A serious limitation of these materials is that carbon reacts with oxygen; it oxidizes in air at temperatures above 425°C. To improve the oxidation resistance of carbon-carbon composites, chemical sources for molecularly dispersing boron in the carbon matrix were explored.

The incorporation of boron particles which react with oxygen to form boron oxide glass and seal the surface of the carbon-carbon, has been used, but the distribution of boron in these carbon-carbon materials has not been uniform. Added as particulate to prepreg cloths, but not into the resin or liquid pitch precursors used for impregnation (due to viscosity limitations), results in boron concentrated in fiber rich areas. This leaves large amounts of the carbon matrix devoid of boron and susceptible to oxidation. Molecularly dispersed boron, provided in the impregnate, was proposed for this effort as a means to improve the oxidation resistance of the inhibited carbon-carbons.

The molecular dispersion of boron in the carbon matrix, successfully demonstrated in the Phase I work, was further developed and employed to prepare high performance prepregs, based on PAN carbon fiber reinforcement, for composite fabrication. Resin chemistry was also studied in relation to moisture and oxidation resistance.

Composite fabrication processes, including debulk, autoclave cure, carbonization, graphitization and densifications, were developed based upon TGA and DSC results. Boron modified carbon-carbon composite panels were fabricated via the optimized technique. Physical and mechanical properties of this modified composite were determined and compared with that of an unmodified baseline material. Finally, the oxidation resistance of the modified composites was assessed, with and without a protective SiC coating.

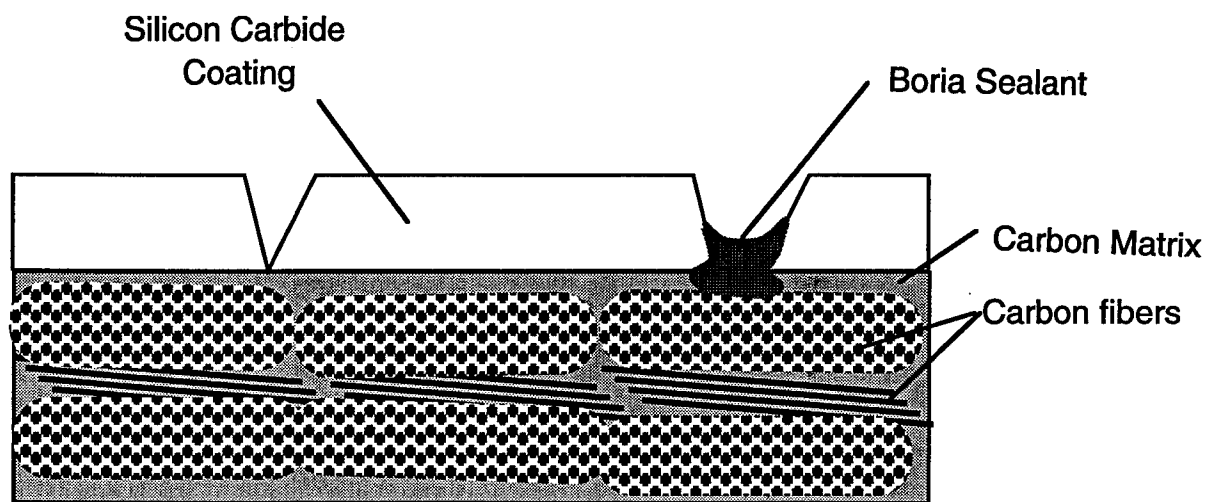
### 1.1 Background

Oxidation inhibited graphitic materials have been studied for selected aerospace applications for over 30 years. Reentry vehicle nose tips and rocket nozzle inserts were the main applications in these early R&D programs. Although development efforts have been fairly successful at reducing oxidative consumption, the resulting materials are often mechanically unsuitable for complex thermo-structural environments, similarly to bulk graphite or ceramics.

In the early 1970's, carbon-carbons consisting of low modulus rayon based carbon fibers were developed for the leading edges of the space shuttle. Pack cementation reactions of the composites with silicon and overlays of silica sealants from TEOS were used to mediate oxidation. However, demands for higher performance required for aircraft structures, gas turbine engines and hot aerospace structures resulted in development activities concerning both the constituent materials and the process. High performance PAN based carbon fibers have since been used for the reinforcement, and complicated oxidation protection systems have been developed.

### 1.2 State-of-the-Art Oxidation Protective System

Figure 1 shows some of the basic elements of oxidation protection system concepts that are currently being investigated for protecting carbon-carbon composites. These include oxidation inhibitors in the composite matrix to slow oxidation once oxygen has penetrated the protective surface coating through flaws and/or coating cracks. Some concepts include treatment of the surface before depositing the first layer of protective coating. This is to improve the adhesion between the coating and substrate. It also reduces the thermal expansion mismatch between coating and substrate. Most coatings are silicon based. Some concepts include a glaze over the outlayer to seal cracks that develop during the cooling step in processing.



**Figure 1. State-Of-The-Art Inhibited Carbon-Carbon System**

#### 1.2.1 Surface coating

Ceramic coatings developed for carbon-carbon substrates to date are primarily silicon based (silicon carbide or silicon nitride). These silicon based ceramics have the best thermal expansion compatibility and exhibit the lowest oxidation rates of the high temperature ceramics. Silicon carbide coatings are formed by deposition onto a suitable substrate using either a pack cementation or a chemical vapor deposition (CVD) process. In the pack process, silicon vapor is reacted with the outer surface regime of carbon-carbon to form silicon carbide. A typical process consists of pack mixture of 30, 30 and 40% of fine alumina, silicon carbide and silicon powders respectively and a 4 hour heat treatment at 1700°C. Coating thicknesses nominally vary between 0.015 and 0.030 inch. Thicker coatings tend to decrease coating-substrate adherence while coatings over 0.1 inch thick are prone to spalling during thermal cycling. To maintain acceptable mechanical properties, the pack treated parts must have a thickness over 0.065 inch.

In CVD, a solid material is deposited from gaseous precursors onto a heated substrate. SiC is commonly deposited from methyltrichlorosilane onto carbon-carbon in the presence of hydrogen. Process conditions can be varied significantly to alter the coating chemistry, thickness, microstructure and properties. The CVD process is also used to form silicon nitride based coatings. Deposition temperatures of SiC and Si<sub>3</sub>N<sub>4</sub> range from 1000° to 1450°C. As the composite is cooled, residual tensile stress is developed in the coating due to a thermal expansion mismatch between the coating and the substrate.

The primary mechanism of oxidation protection for both SiC and Si<sub>3</sub>N<sub>4</sub> is the formation of a surface film of amorphous silica that impedes the transport of oxidizing species to the underlying carbon-carbon substrate. Although the oxidation kinetics of both coating compositions is similar, Si<sub>3</sub>N<sub>4</sub> coatings are favored sometime because of their lower expansion coefficient and better resistance to thermal shock.

Capabilities of silicon-based coatings depend greatly upon their stoichiometry and environmental conditions. For CVD deposited coatings of SiC and Si<sub>3</sub>N<sub>4</sub>, the upper use temperature is defined by reactions at the interface between the SiO<sub>2</sub> scale and the underlying ceramics. The maximum long-life temperature capability of stoichiometric SiC and Si<sub>3</sub>N<sub>4</sub> coatings are about 1660° and 1820°C, respectively.<sup>1</sup> Above these temperatures, reaction between the silica scale and the SiC or Si<sub>3</sub>N<sub>4</sub> substrate creates SiO and CO gas pressures exceeding ambient conditions, and results in failure of the coating.

### 1.2.2 Sealant

Various glassy sealants have been developed for overcoating the silicon-based material and filling the coating cracks. The carbon-carbon composite has a substantially lower thermal expansion coefficient within fiber reinforced lamina than any ceramic with symmetric crystal structure. As coatings are cooled from their peak process temperature, the induced tensile residual stresses cause the material to crack. At temperatures below 1000°C, the cracks remain open and substrate oxidizes. Hence, some form of protection is required for the temperature range between 400° to 1000°C regime. At temperatures above 1000°C, the cracks are mechanically closed and chemically sealed by oxide formation.

The sealant processes employed are either vacuum deposition or brush application. Boron carbide CVD coating or boron particle containing resins are applied onto the substrate before the surface coating. Glass formers are used in the fabrication of the composites, rather than the oxide glasses themselves. The use of precursors facilitates processing of the composites and results in a large in-situ volume expansion when the glass is formed by exposure to oxygen. This is beneficial because a large volume increase in a confined space will force the glass to flow into adjacent cracks and pores. Important characteristics of glass sealant for effective carbon-carbon protection include surface energy, viscosity, thermal stability and oxygen permeability. Pure P<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> exhibit surface energy values of 100 mJ/m<sup>2</sup> or less over the temperature range of interest, while GeO<sub>2</sub> and SiO<sub>2</sub> have values of 250 to 300 mJ/m<sup>2</sup>.<sup>2,3</sup> Because the carbon has very low surface energy, it has long been recognized that borate and phosphate glasses are most effective for forming thin, well adherent layers to protect against oxidation.<sup>4</sup> The surface energy of SiC is

significantly greater than carbon and wetting by the glasses is generally not a problem.

Glasses used for protecting carbon-carbon composites should be chemically stable with carbon and have low vapor pressures in the temperature range of interest. High vapor pressure limits the use of  $P_2O_5$  to temperatures below  $316^\circ\text{C}$  ( $600^\circ\text{F}$ ) while  $SiO_2$  is useful to over  $1649^\circ\text{C}$  ( $3000^\circ\text{F}$ ).  $B_2O_3$  and  $GeO_2$  lie between these extremes.<sup>6,7</sup> Volatilization of  $B_2O_3$  and  $GeO_2$  upon extended exposure to temperatures above  $1371^\circ\text{C}$  ( $2500^\circ\text{F}$ ) is a concern, especially in moist environments.

Viscosity of the glass is critical for its efficacy in oxidation protection. Low viscosities ( $10^3$  to  $10^6$  poise) are required to fill and seal cracks, and only borate glass meets this requirement.  $P_2O_5$ ,  $GeO_2$  and  $SiO_2$  all have viscosities which are too high. Thus most of the sealants used are boron-based because of their low melting temperature, low viscosity in the molten state and ability to wet the carbonaceous surfaces. The melting points of these sealants are about  $650^\circ\text{C}$ , thus the substrate remains exposed to oxidation between  $400^\circ$  and  $650^\circ\text{C}$ .

### 1.2.3 Inhibited Substrate

The probability of developing a full-life, completely protective external coating system, based on the aforementioned argument, is very low. The carbon-carbon substrate material will need an inhibitor to act as a safety net against catastrophic oxidation if the coatings fail. Particulate addition, mainly boron and  $ZrB_2$  that form boron-based glasses upon oxidation, has been the major emphasis of the inhibition work on carbon-carbon.

The addition of particulate generally improves the shear properties and decreases the tensile properties of the carbon-carbon composites. A maximum useful particle size is established at about 40 microns. Large particles cause problems during the prepreg operations and are less reactive.

## 1.3 Deficiencies of the Current System

The distribution of the boron (or  $B_2O_3$ ) is not uniform, considering the process of the inhibited substrate. No boron was added into the resin or liquid pitch precursors used for impregnation since the additions would raise the viscosity of the impregnant to unmanageable levels. The amorphous, boron lean matrix that results then suffers severe oxidation when the protective coatings fail. Thus oxidation inhibition of these impregnated matrices, through a chemically modified matrix-forming resin is critical for the success of the development of a long-life oxidation resistant carbon-carbon.

Boron-based sealant performance is limited by several problems. The glass may devitrify and then react unfavorably with other adjacent materials. Most importantly,  $B_2O_3$  is unstable: glasses high in  $B_2O_3$  degrade by hydrolysis under ambient conditions.

Hydrolysis of  $B_2O_3$  results in the formation of ortho-boric acid ( $H_3BO_3$ ) at low temperatures.<sup>8</sup> Conversion of  $B_2O_3$  to  $H_3BO_3$  produces a volume increase of about 125%. This large expansion can cause coating spallation at room temperature.

Heating  $\text{H}_3\text{BO}_3$  above  $100^\circ\text{C}$  results in the release of water vapor and the formation of meta-boric acid ( $\text{HBO}_2$ ). Above  $250^\circ\text{C}$ ,  $\text{HBO}_2$  begins to transform to  $\text{B}_2\text{O}_3$  with the release of water vapor. The absorbed water converts to steam under rapid heating, aggravates the localized stress problem and provides additional oxidizing species.

Alkali addition improves the moisture resistance of  $\text{B}_2\text{O}_3$ .<sup>9</sup> For example, the addition of 20 mole % of  $\text{Li}_2\text{O}$  reduces the leaching rate of  $\text{B}_2\text{O}_3$  by two orders of magnitude.<sup>10</sup> Unfortunately lithium oxide compounds, the least volatile and most stable alkali oxide, are not stable within boron-modified carbon-carbon composites at even minimal processing temperatures. Alkaline earth additions can also benefit the moisture resistance of  $\text{B}_2\text{O}_3$ . A 20 mole %  $\text{CaO}$  addition was found to be very resistant to hydration and leaching.<sup>8</sup> Calcia, which can be added to composites may be relied upon solely to provide the moisture resistance.

#### 1.4 Technical Objectives

The general objective of the proposed Phase II program was to develop a fabrication process of oxidation resistant carbon-carbon composite through molecularly dispersed boron. The effects of the process parameters on the physical and mechanical properties, and most importantly, the oxidation resistance of the composites were determined. Specific objectives of the program are as follows:

- Optimized boron incorporation through manipulation of resin/carborane chemistry.
- Improved moisture resistance through resin chemistry and/or with molecularly dispersed calcium.
- Optimized the fabrication processes and densification with respect to physical properties and oxidation performance.
- Demonstrated that this chemistry is easily incorporated within standard processes through the fabrication of a prototype component.

## 2. Results and Discussion

### 2.1 Chemistry of Carbon-Carborane

#### 2.1.1 Carborane Retention

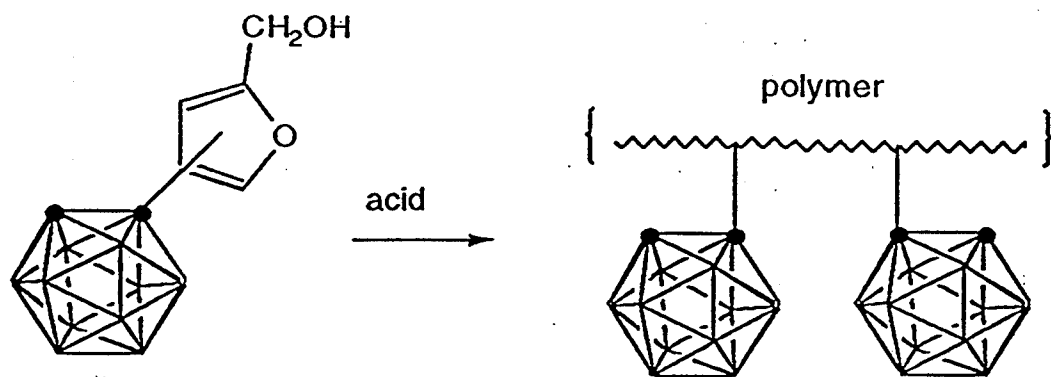
Scanning Auger Microscopy work of the carborane char in Phase I indicated that about 40 wt% carborane sublimed during the carbonization. These results indicated that a better understanding of the chemistry of carborane and the curing process would help minimize carborane loss during the carbonization process. Since carborane is a relatively expensive chemical, reduced sublimation losses would be help in reducing the cost of the inhibited composites.

Improving the boron retention rate through chemical structure modifications of carborane is difficult due to its thermochemical characteristics. Carborane does not decompose at temperatures below 600°C.<sup>11</sup> Ortho-carborane transforms into meta-carborane at temperatures around 450°C. This meta isomer changes to para-carborane at 600°C. No published results on the decomposition mechanism of carborane at temperatures greater than 600°C is currently available.

The carborane molecule was successfully modified to improve its solubility in phenolics in Phase I through ligand additions at Princeton University. Addition of carboxylic acid significantly improved the solubility of carborane in phenolics due to a better match in chemical structure. However, ligand modifications through attachments of naphthyl ether and carboxylic acid phenyl in Phase I did not affect the boron retention. Also, since additions of functional groups reduce the boron content of the carborane molecules while increasing cost, carborane retention rate must be significantly improved to warrant modification of the carborane molecule.

#### 2.1.1.1 Synthesis of Carborane-Furan Molecules

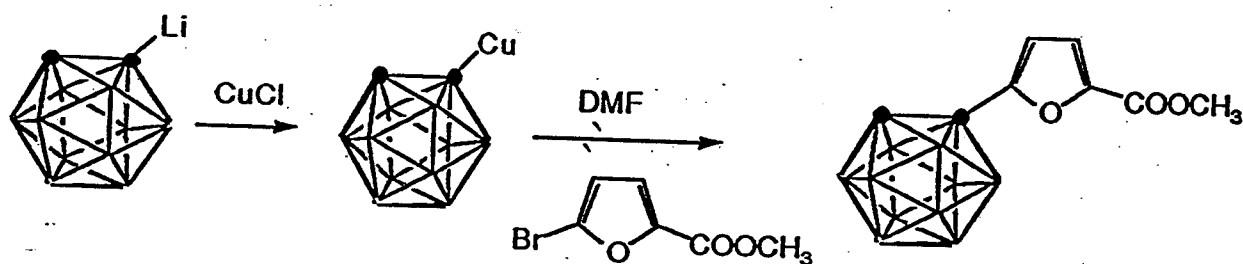
Direct attachment of the carborane to a phenol or furfuryldehyde group was also tried at Princeton University to improve the retention of carborane. The carborane-phenol or carborane-furfuryldehyde should participate directly in the polymerization process prior to carbonization, forming a link between the carborane and the carbon-carbon matrix (Figure 2).



**Figure 2. Schematic of Boron Retention Through Furan Attachment**

The carborane-furfuryl monomer (5-(1-*o*-Carboranyl)-2-furoic acid methyl ester) was prepared by incorporating a modified furan with carbonyl copper through a coupling reaction (Figure 3). To a solution of *o*-carborane (0.94 g, 6.5 mmol) in dry ether (8 ml), 2.5 M solution of *n*-butyllithium in hexanes (2.6 ml) was added at 0-5 °C with stirring. The mixture was stirred at room temperature for another 1 hour and cooled to -20°C. Then a suspension of copper (I) chloride (0.64 g, 6.5 mmol) in dry THF (14 ml) was

added under argon. The mixture was stirred at room temperature for 2 hours, then at 40°C for 10 minutes. A solution of 5-bromofuroic acid methyl ester (1.33 g, 65 mmol) in DMF (15 ml) was added, and excess volatile solvents distilled until the temperature of the mixture reached 110°C. After stirring at this temperature for 3 hours, the mixture was cooled, poured into 5% HCl (30 ml) and extracted with ether. The ether extract was washed with water, dried over  $\text{MgSO}_4$  and evaporated to give 1.29 g of the dark oil which was mostly polymers and starting materials. About 0.03 g of 5-(1-o-Carboranyl)-2-furoic acid methyl ester was isolated by column chromatography on silica gel with chloroform.



**Figure 3. Schematic of the Synthesis of Carborane-Furan Monomer**

The yield of the carborane-furan monomer was only 1.7%. Unless the yield of the carborane-furan monomer can be significantly increased, direct attachment of the carborane to furfuryl will not be cost effective. Several factors contributed to this low yield. First, some of the starting carborane was wasted through formation of dilithio and dicopper compounds. This can be easily avoided by blocking of the second cage carbon. Second, the yield was significantly reduced by polymerization in the formation step. Finally, the bromo compound was not ideal. An iodide compound would be better for the coupling reaction as it allows a lower reaction temperature that minimizes polymerization. Based on these hypotheses, several reactions were attempted without success.

- a. Reaction of 1-lithio-2-tert-butyldimethylsilyl-o-carborane and 2-iodo-5-tert-butyldimethylsilyloxymethyl furan

Reaction of the title compounds either in ether or THF solution at 20-70°C over 2-72h produced no coupling product. Instead, 1-iodo-2-tert-butyldimethylsilyl-o-carborane and 2-tert-butyldimethylsilyloxymethylfuran were obtained.



- b. Reaction of 1-bromomethyl-*o*-carborane and 2-lithio-5-tert-butyltrimethylsiloxymethyl furan

Reaction of the title compounds in ether at room temperature or reflux gave no coupling products. The main product after 30h reflux was 1-methyl-*o*-carborane. Most of the furan compound polymerized.

- c. Attempt coupling of 1-bromo-2-tert-butyltrimethylsilyl-*o*-carborane or 1-bromo-2-methyl-*o*-carborane with 2-furyl zinc chloride

No reaction was detected between each of the title compounds and 2-furyl zinc chloride in THF in the presence of *tetrakis* (triphenylphosphine)palladium as a catalyst at 50°C after 30h.

- d. Reaction of 1-lithio-2-tert-butyltrimethylsilyl-*o*-carborane and 2-iodofuran

The traces of the coupling product- 1-furyl-2-tert-butyltrimethylsilyl-*o*-carborane were detected after addition of 2-iodofuran solution in THF to lithio compound in ether at -30°C. No further accumulation of the product was found after several hours at room temperature or reflux for 4h. Addition of TMEDA did not influence the reaction. A lot of polymer tars were formed.

- e. Reaction of 1-methyl-*o*-carborane-2 copper and 2-iodofuran

Reaction of the title compounds in THF-DMF solution after 30h at 70°C gave around 10% conversion of the copper compound into 1-methyl-2-iodocarborane. No coupling products were found.

- f. Reaction of 1-tert-butyltrimethylsilyl-*o*-carborane-2 copper and 2-iodofuran

No coupling products were found in THF at reflux. Some 1-iodo-2-tert-butyltrimethylsilyl-*o*-carborane was detected by GC/MS. Reaction in THF-DMF at 70°C caused desilylation. After 24h the mixture contained no silylated compound. Mostly *o*-carborane with the admixture of the coupling product 1-furyl-*o*-carborane was formed.

- g. Reaction of *o*-carboranyl copper and 2-iodofuran

To a suspension of *o*-carboranyl-1 copper prepared as aforementioned from *o*-carborane (5.87 g, 40 mmol) in ether (60 ml), 1.6M butyllithium in hexanes (25 ml) and copper (I) chloride (5 g, 50mmol) in dry THF (100 ml) a solution of 2-iodofuran (7.8 g, 40mmol) in DMF (70 ml) was added. Most volatile solvents were distilled in an argon stream until the temperature of the refluxing mixture reached 80°C. The mixture was stirred at this temperature for 24h, cooled, poured into 5% HCl (100 ml), extracted with ether, dried over magnesium sulfate and evaporated. The dark brown oil thus obtained contained 2 volatile compounds: *o*-carborane (55%) and 1-furyl-*o*-carborane (45%), and a lot of polymers. Attempts to purify the

coupling product by sublimation and /or column chromatography were unsuccessful. Fast polymerization contaminated any samples of 1-furyl-*o*-carborane by a number of products.

Synthesis of furylcarborane proved to be very difficult. The coupling product formation in the case of *o*-carboranes/2-substituted furans is extremely sensitive to the electronic effect of the substituents, in sharp contrast to well known aromatic/heteroaromatic reactions. No coupling product was found for 1-methyl-*o*-carborane and 1-tert-butyldimethylsilyl-*o*-carborane reactions. 2-tert-Butyldimethylsiloxymethyl furan derivatives appeared to be inactive for coupling with carboranes. Only unsubstituted *o*-carboranyl copper reactions with 2-iodofuran or 5-bromofuroic acid methyl ester produced some amount of furylcarborane derivatives which are the major products in the initial stages of reaction. However, both coupling products: 1-furyl-*o*-carborane and 5-(1-*o*-carboranyl)-2-furoic acid methyl ester are sensitive to polymerization. This led to a substantial transformation into tars in the reaction mixture and/or during the usual work up and purification procedures, making the yield of desired product far less than satisfactory.

#### 2.1.1.2 Modifications of Resin Systems

Modifications of the resin system was also investigated as a another way to retain carborane. Study of carborane additions in phenolic and furan resins by Baicher indicated that furfuryl retained all the carborane added after a 1000°C carbonization process, with 2% *o*-carborane addition.<sup>12</sup> The high retention of carborane was attributed to the formation of solid linkages during a low temperature cure. This 2% carborane addition also increased the char yield of furfural resin by 18%.

To study the retention of carborane in different resin systems, a fixed amount of *o*-carborane (5 wt%) was added into various resins separately. The carborane added resins were cured and carbonized, using the processes recommended by the manufactures or developed during Phase I. The boron content or retention of these chars was determined by elemental analysis. The resin systems studied in the Phase II program included phenolic, furfuryl and Code88A, a standard pitch resin system used by Kaiser.

A 0.57 wt% of oxalic acid was used to cure a 5 wt% carborane added furfuryl/resorcinol (60/40 by weight) mixture. Curing was carried out in two stages (50° and 125°C). The cured sample was carbonized at 900°C under a nitrogen atmosphere. Cure and carbonization yields of this sample were determined to be about 92.7 and 65.7% respectively. With these yields, the theoretical boron content of the carbonized char was calculated to be about 5.85 wt%. The actual boron content of this sample was measured to be about 3.84 wt% by Galbraith Laboratories, Knoxville, TN. This corresponds to about 34% loss of boron (Table 1). The furfuryl sample did not show the reported retention of carborane.

**Table 1. Boron Retention Rates of Carbon Precursors  
5% Carborane Modified**

	<u>Furfuryl</u>	<u>SC1008</u>	<u>Ca-OM</u>	<u>Code88A</u>
Cure Yield (%)	92.7	74.6	71.0	73.0
Carb Yield (%)	65.7	73.2	68.5	71.0
Total Yield (%)	61.0	54.6	48.7	52.0
Theoretical B(wt.%)	5.85	6.88	7.70	7.21
Actual Ca(wt.%)	-	-	5.08	-
Actual B(wt.%)	3.86	3.91	5.79	5.19
Boron Loss (%)	34	43	25	28

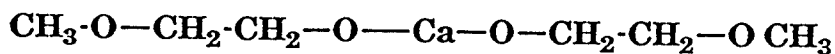
Ca-OM : Calcium organometallic compound added SC1008 phenolic

In a separate study funded by NASA Langley, calcium additions to the phenolic resin showed complete boron retention.<sup>13</sup> The calcium was added through direct interaction between calcium metal and phenolic resin. This calcium modified phenolic char also showed promise in moisture resistance.

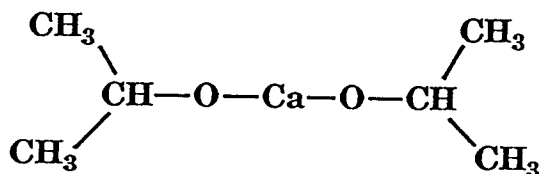
#### 2.1.2 Moisture Resistant Additives

Moisture sensitivity of the boron modified system was highlighted in the TGA oxidation tests during the Phase I work. Alkali and alkaline earth additions had been shown to improve the moisture resistance of B<sub>2</sub>O<sub>3</sub>. Calcium addition, through the addition of Ca-2-ethyl hexanote, reduced the moisture attack significantly. There is only about 3% Ca in this compound. Calcium rich compounds were also examined to reduce moisture attack on the boron added carbon-carbon composites.

Complete protection of the B<sub>2</sub>O<sub>3</sub> glass requires about 30 mole% of CaO, which corresponds to about 5 wt% of calcium addition in the resin. To achieve this concentration, an isopropanol soluble, high Ca content molecule is required. Calcium iso-propoxide, a chemical with a Ca content of over 25 wt% and soluble in isopropanol, was chosen as an ideal candidate for this task. Calcium iso-propoxide was synthesized and added to the carborane modified system. Calcium methoxyethoxide, a commercially available and inexpensive high calcium content chemical, was also evaluated as a calcium precursor (Figure 4).



Calcium Methoxyethoxide



Calcium Isopropoxide

**Figure 4. Chemical Structures of Calcium Precursors**

#### 2.1.2.1 Synthesis of Ca-Isopropoxide

About 0.45 g (11 mmol) of calcium turnings was added to a Schlenk tube in a glove box. After addition of 20 mL of isopropanol, the tube was removed to the hood. The mixture was cooled to -78 °C in acetone/dry ice and then NH<sub>3</sub> was condensed in. This caused the calcium to react. After approximately 1 hr the mixture was allowed to warm up, leading to more rapid reaction of the calcium. An additional 30 mL of isopropanol was added as the suspension had started to gel. The mixture was left stirring over night.

Unreacted calcium and much undissolved solid was left in the vessel, so another 10 ml of isopropanol were added. Most of the calcium appeared to have reacted, but significant amounts of suspended white solid had not dissolved.

This mixture was added to a sample of phenolic (previously charged with carborane such that B = .044 mol). Only about 15 ml of this suspension dissolved in the phenolic, after which time an insoluble white solid persisted. Calcium isopropoxide has limited solubility in isopropanol, and the suspension has limited solubility in the phenolic resin.

#### 2.1.2.2 Ca-Organometallic Addition

Calcium-methoxyethoxide (20% in methoxyethanol) was also used to provide calcium in the 5% carborane added SC1008 resin. A sample of 11 g of phenolic resin which had been charged with 5% carborane (total B = .04 mol) was placed in a 125 ml Wheaton bottle. The phenolic resin was purged with N<sub>2</sub> for 10 min and then taken into the glove box along with a solution of bis(methoxyethoxy)calcium in methoxyethanol (Gelest). The required amount of Ca solution (9.5 g of 20 wt % solution = .01 mol Ca) was titrated into the phenolic resin. At times a white solid would collect at the surface of the resin, but was easily swirled away. The resulting, slightly more orange, resin was transparent after the addition was complete.

To prevent the precipitation of calcium from reaction with moisture, curing of this mixture was carried out under nitrogen atmosphere until the mixture was solidified. After a 125°C cure in air, the sample was carbonized at 900°C. The sample foamed during the carbonization. This foaming was believed to be attributed to the residual methoxyethanol solvent. Disregarding the residual solvent, the carbon char would have a theoretical boron and calcium content of 7.7% for each element. Elemental analysis of this sample showed a 5.79 and 5.08 wt% of boron and calcium, respectively. Based on these results, the boron retention was calculated to be about 75% (Table 1). The retention rate may have been lower, if the amount of residual solvent was accounted for.

Since none of the calcium organometallic compounds studied were promising in providing calcium for moisture resistance, no calcium was added in the carborane modified SC1008 phenolic resin during the preparation of preregs. Such a moisture sensitive matrix would affect the performance of carborane modified carbon-carbon composites. Fortunately, the Code88A liquid pitch that was chosen as the impregnant does not suffer moisture attack. (See section 2.2.2)

The problem of moisture sensitivity in the prepreg can be solved by direct reaction between calcium metal and phenolic resin. However, incorporation of calcium through reaction is not cost effective due to the extremely slow reaction rate. The reaction rate is limited by the temperature limits allowable for phenolic resin. To enhance the efficiency of calcium incorporation, a fine calcium powder can be added to the phenolic resin to increase the reaction rate. The calcium surface area, and reactivity, can be significantly increased by particle size reduction. Ammonia can also be used as a catalyst to expedite the reaction between calcium and the phenolic resin.

## 2. 2 Characterization of Boron Modified Resin Chars

### 2.2.1 Distribution and Compositional State of Boron

The distribution of boron and the oxidation states present in the glassy carbon were determined using ESCA spectrometer. This work was performed at Evans East, Plainsboro, New Jersey by Mr. Jeff Shallenberger.

A Perkin-Elmer 5000LS with monochromatic aluminum X-ray source was used for this study. All samples were examined initially with low resolution survey scans to determine which elements were present. High resolution ESCA multiplex data were taken to determine the atomic concentration and binding energy of the elements requested. The quantitation of the elements was accomplished by using the atomic sensitivity factors for a Perkin-Elmer, PHI Model 5000LS ESCA spectrometer as configured. The approximate sampling depth for these experiments was 50 Å relative to carbon electrons.

The results of the quantitation from the high resolution multiplex spectra and the survey spectra are given in Table 2 for the samples both as received and after sputtering ~ 1,000Å. In addition to the C, O, B and Ca expected on the samples, Mo, S and Si were detected on all of the samples. Minor amounts of calcium were detected

on the furfuryl samples, for which high resolution spectra were not requested. Argon sputtering increased the boron and carbon content, except for the calcium organometallic added phenolic sample, presumably by removing surface contaminants. Code88A sample, with addition of coal tar pitch, shows a significantly lower amount of oxygen and a high carbon content after sputtering.

**Table 2. Atomic Concentration of Elements Detected**

<u>Sample</u>	<u>Acq. Type</u>	<u>O</u>	<u>Ca</u>	<u>C</u>	<u>B</u>	<u>Mo</u>	<u>S</u>	<u>Si</u>
Furfuryl, AR	H.Res.	17.5	-	80.4	2.1	-	-	-
Furfuryl, AR	Surv.	15.9	0.6	79.6	2.2	0.3	0.1	1.3
Furfuryl, SP	H.Res.	12.1	-	83.6	4.3	-	-	-
Furfuryl, SP	Surv.	11.0	0.7	83.3	4.2	<0.1	0.2	0.5
Ca-OM, AR	H.Res.	18.7	1.8	78.4	1.2	-	-	-
Ca-OM, AR	Surv.	17.6	2.0	76.8	1.0	0.5	0.6	1.5
Ca-OM, SP	H.Res.	22.3	6.5	63.4	7.8	-	-	-
Ca-OM, SP	Surv.	21.0	6.9	63.5	8.3	<0.1	0.0	0.3
Code88A, AR	H.Res.	18.6	-	80.5	0.9	-	-	-
Code88A, AR	Surv.	17.2	0.2	76.1	1.2	0.2	1.1	3.4
Code88A, SP	H.Res.	4.4	-	92.0	3.6	-	-	-
Code88A, SP	Surv.	4.1	0.0	92.7	2.7	0.0	0.3	<0.1

AR = as received

SP = sputtered

H.Res. = high resolution multiplex

Surv. = low resolution survey scan

Ca-OM = Ca-organometallic added phenolic resin

The calcium organometallic sample contained the highest amounts of oxidized calcium and boron species. It also suggests a much higher calcium content (atomic%) than the wt% calcium determined by elemental analyses using the ICP technique. Calcium distribution in this sample may not be uniform.

Calcium was present initially as CaO and did not appear to change with sputtering. Calcium oxide and calcium carbonate are virtually indistinguishable from their Ca 2p spectra alone. The CaO identification comes by way of elimination of CaCO<sub>3</sub> as a possible species using both the atomic concentrations and the curve fits of calcium organometallic added phenolic sample. If calcium were present as CaCO<sub>3</sub> then one would expect three oxygens for each calcium. The O/Ca ratio is roughly 3:1, but there is also oxygen associated with boron and carbon (C-O, C=O, etc.). Furthermore, there is no carbonate peak in the C 1s spectra; only the carbon peak at 284.6 eV was detected. Also, no B<sub>4</sub>C peak at 281.8 eV was detected.

The boron chemistry changed with sputtering: from a single  $B_2O_3$  peak at the surface to a mixture of  $B_2O_3$  and boron sub-oxide ( $BO_x$ ) below the surface. Figures 5 to 7 show the B 1s curve fit of these materials, using a Gaussian-Lorentzian peak profile, and a summary is given in Table 3. Although some oxides can be reduced by sputtering,  $B_2O_3$  is not believed to be reduced by the ion beam used in this sputtering.

In general, all samples contained the same types of functional groups but the amounts varied drastically from sample to sample. Calcium organometallic added phenolic char had relatively high percentage, while Code88A sample had a much lower percentage, of  $B_2O_3$  (sputtered) in comparison to the other samples. This is consistent with the oxygen contents detected in these samples, as shown in Table 3. Both boron and calcium were oxidized at the surface and into the bulk of the samples. Boron did not appear to be fully oxidized in the bulk.

**Table 3.**

**Atomic Concentrations of Boron Species  
from B 1s Curve Fits**

<u>Sample</u>	<u>B1</u>	<u>(eV)</u>	<u>B2</u>	<u>(eV)</u>	<u>B3</u>	<u>(eV)</u>	<u>B4</u>	<u>(eV)</u>
Ca-OM, AR	-	-	100.0	192.0	-	-	-	-
Ca-OM, SP	-	-	67.6	191.9	26.8	190.6	5.6	189.0
Code88A, AR	-	-	100.0	192.2	-	-	-	-
Code88A, SP	6.8	194.4	25.0	192.3	40.3	190.4	27.8	188.5
Furfuryl, AR	-	-	100.0	192.0	-	-	-	-
Furfuryl, SP	4.5	194.2	55.3	192.5	26.3	190.8	14.0	189.0

B1 = charged  $B_2O_3$

B2 =  $B_2O_3$

B3 =  $BO_x$

B4 =  $BO_y$ , where  $1.5 > x > y$

B 1s references:

<u>Species</u>	<u>Energy</u>
$B_2O_3$	192.0-193.3
$H_3BO_3$	193.0
B	186.5-187.3

ESCA CURVE FIT 7/7/93 ANGLE= 45 deg ACQ TIME=9.26 min  
 FILE: Curve\_Fit 317-07 #4, sputtered  
 SCALE FACTOR= 0.005 k c/s, OFFSET= 0.000 k c/s PASS ENERGY= 35.750 eV Al 600 M

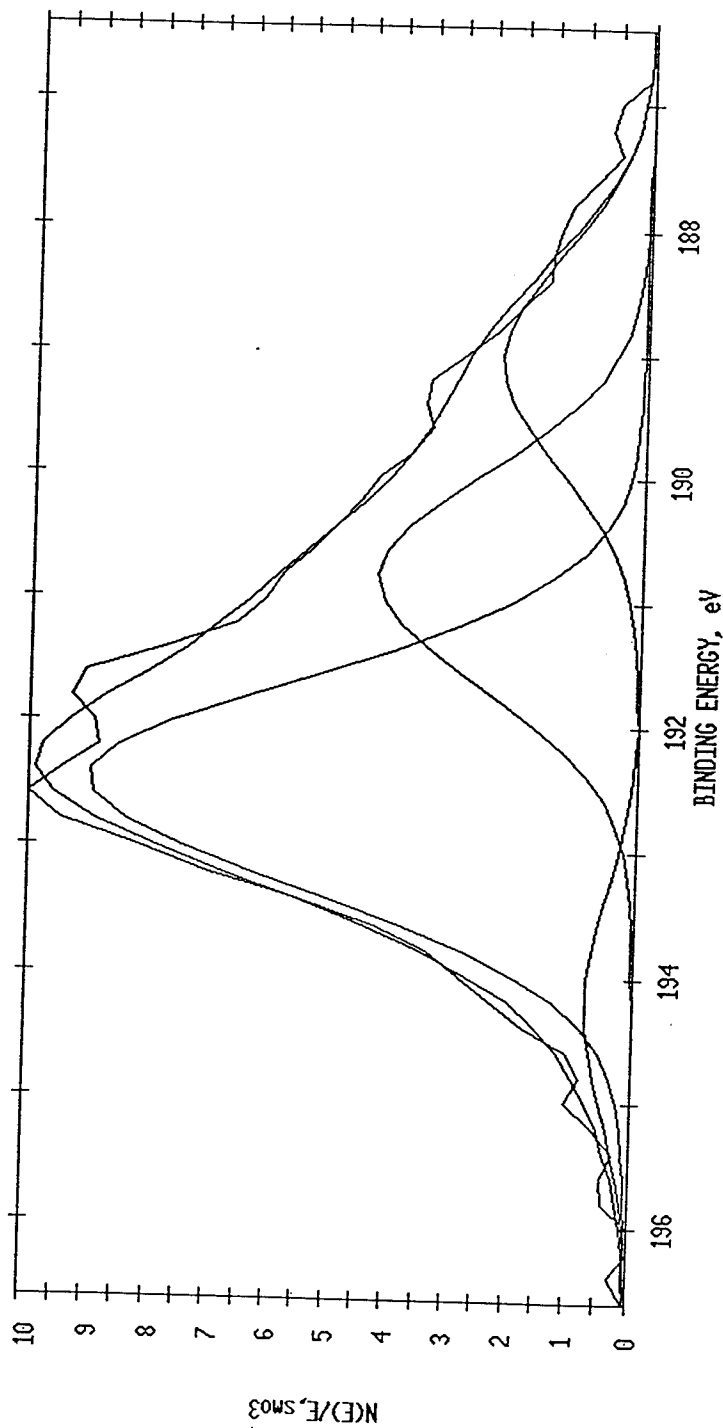


Figure 5. B 1s Curve Fit, Furfuryl, Sputtered



ESCA CURVE FIT 7/7/93 ANGLE= 45 deg ACQ TIME=9.26 min  
 FILE: Curve\_Fit 299-78 #2, sputtered  
 SCALE FACTOR= 0.011 k c/s, OFFSET= 35.750 eV Al 600 W

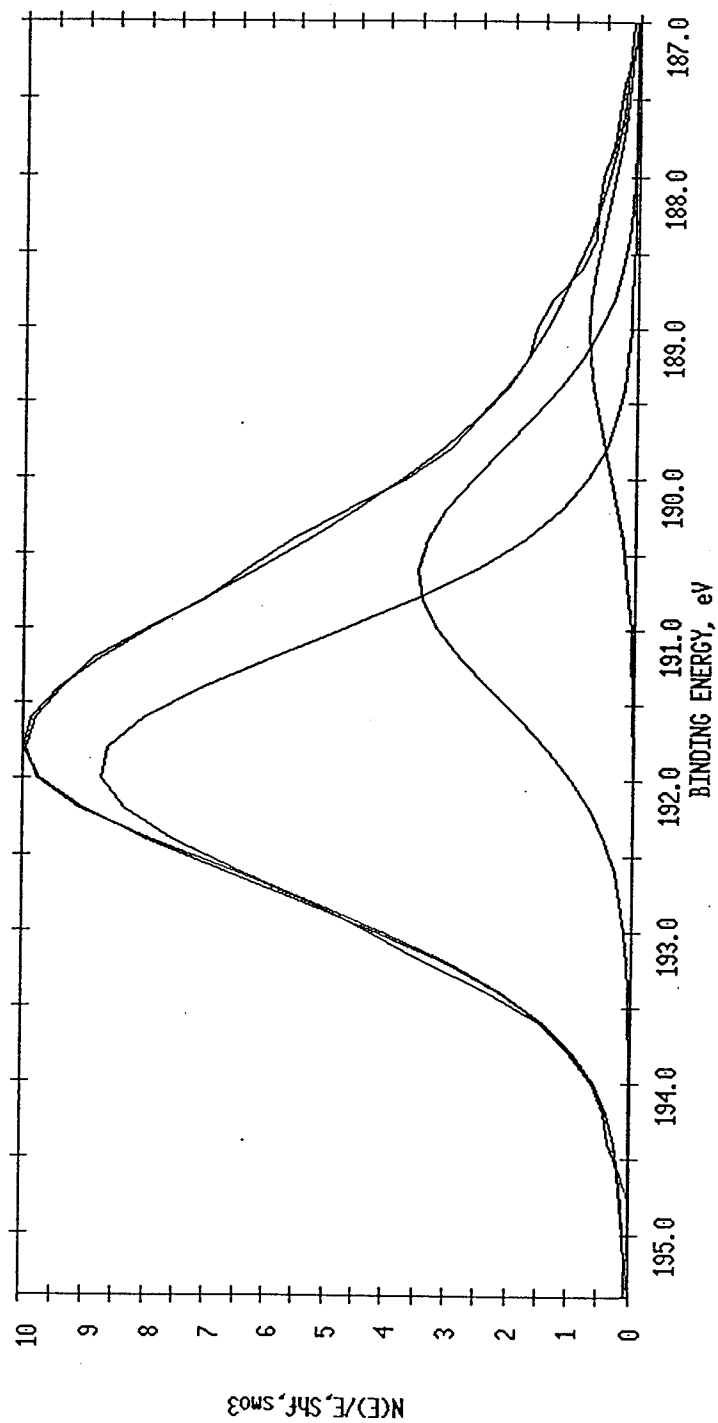


Figure 6. B 1s Curve Fit, Ca-OM, Sputtered

ESCA CURVE FIT 7/7/93 ANGLE= 45 deg ACQ TIME=9.26 min  
 FILE: Curve\_Fit 299-88 #2, sputtered  
 SCALE FACTOR= 0.004 k c/s, OFFSET= 0.000 k c/s PASS ENERGY= 35.750 eV Al 600 W

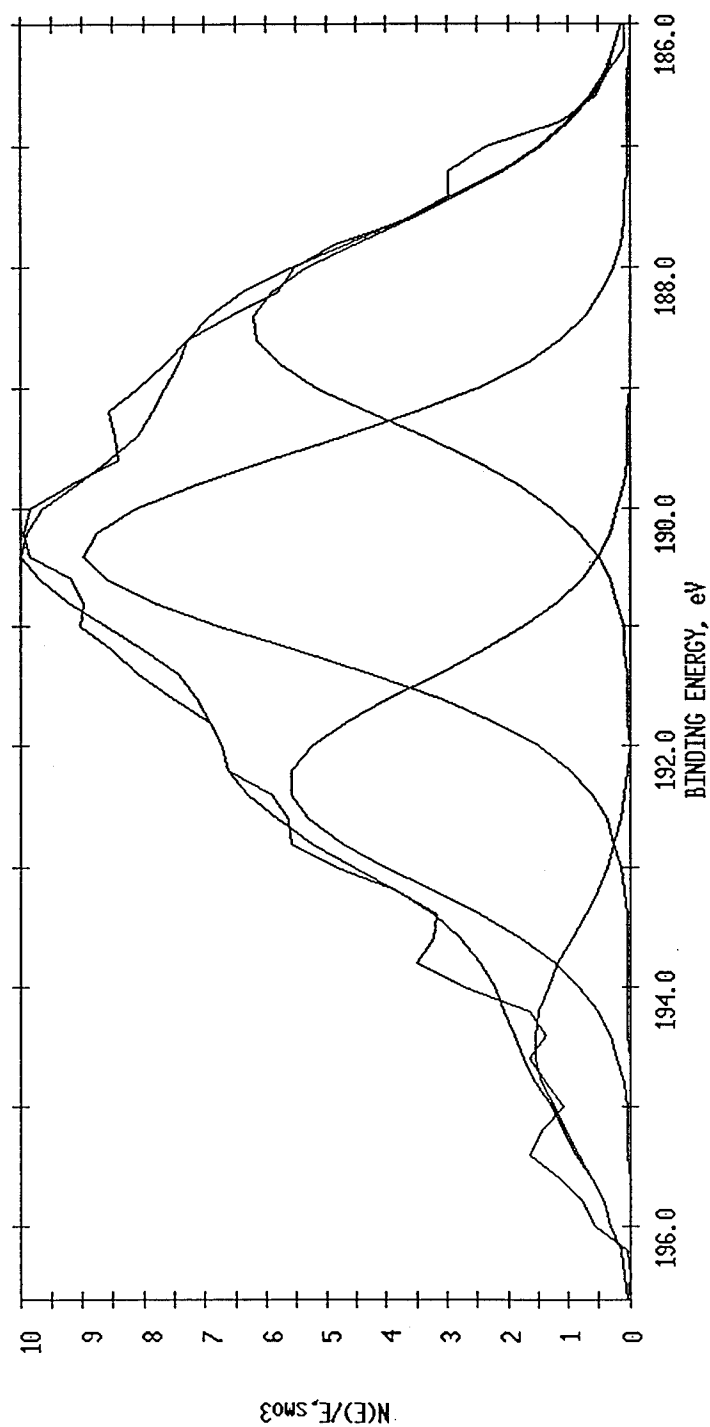


Figure 7. B 1s Curve Fit, Code 88, Sputtered

### 2.2.2 Characterization of Oxidation and Moisture Resistance

The oxidation resistances of the carbon chars were determined by air oxidation at 900°C. This represents the most severe condition as no additional oxidation of the carbon-carbon substrate is expected at higher temperatures due to the re-sealing (mechanically) of protective coatings.<sup>14</sup> Moisture resistances of the carbon chars were determined by monitoring the weight changes after carbonization and oxidation tests. A saturated aqueous solution of sodium bisulfate monohydrate in a desiccator was used to provide a 52% relative humidity at 20°C. Table 4 shows the oxidation and moisture resistances of the 5 wt% carborane modified carbon chars. The calcium organometallic compound added sample, which foamed during the carbonization process, shows a much higher weight loss during the oxidation test and higher weight gain during the exposure test. These results can be attributed to the much higher surface area of the sample.

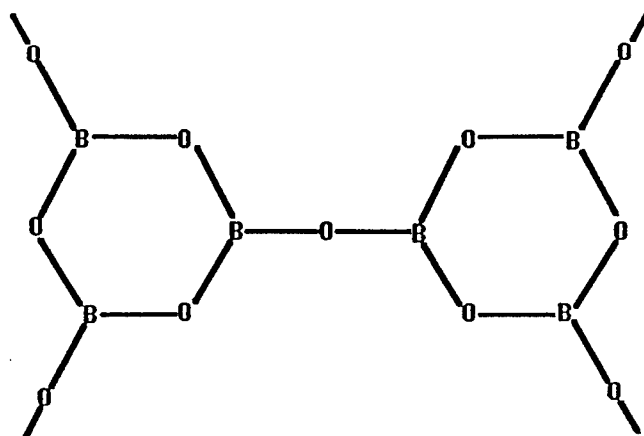
**Table 4. Oxidation and Moisture Resistances of the  
5% Carborane Modified Carbon Chars**

	<u>Furfural</u>	<u>SC1008</u>	<u>Ca-OM</u>	<u>Code88A</u>
Wt.% B	3.86	3.91	5.79	5.19
Wt. Gain (%) after 96 hours	1.10±0.25	2.07±0.10	5.61±0.73	0.29±0.14
Wt. Loss (%) 900°C, 1 hour	9.7	7.2	43.7	4.3

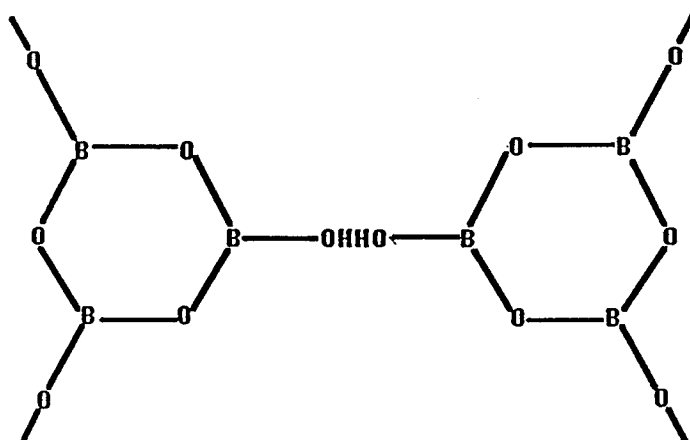
With a similar boron content, furfuryl picked up less moisture than phenolic (SC1008) char. The Code88A char with a higher boron content shows a much lower moisture affinity. All of these chars, except the calcium organometallic compound added sample, show a close relationship between boron content and oxidation resistance.

Vitreous B<sub>2</sub>O<sub>3</sub> is made up of planar triangles of a boron atom bonded to three oxygen atoms (Figure 8).<sup>3</sup> Most of the triangles are arranged in boroxol rings containing three boron atoms and three oxygen atoms. Each oxygen atom is shared by two boron atoms so the rings are connected by oxygen bridges between boron atoms. This produces an open, low density structure.

The polar H<sub>2</sub>O molecules intrude the structure to produce hydrogen bonds between the boron-oxygen links (Figure 9). Addition of an H<sub>2</sub>O to two adjoining BO<sub>3/2</sub> triangles produces two metaboric acids (HBO<sub>2</sub>). Hydrolysis at low temperatures proceeds to completion and H<sub>3</sub>BO<sub>3</sub> is formed.



**Figure 8. Chemical Structure of the 3-Coordinated Boroxol Rings**

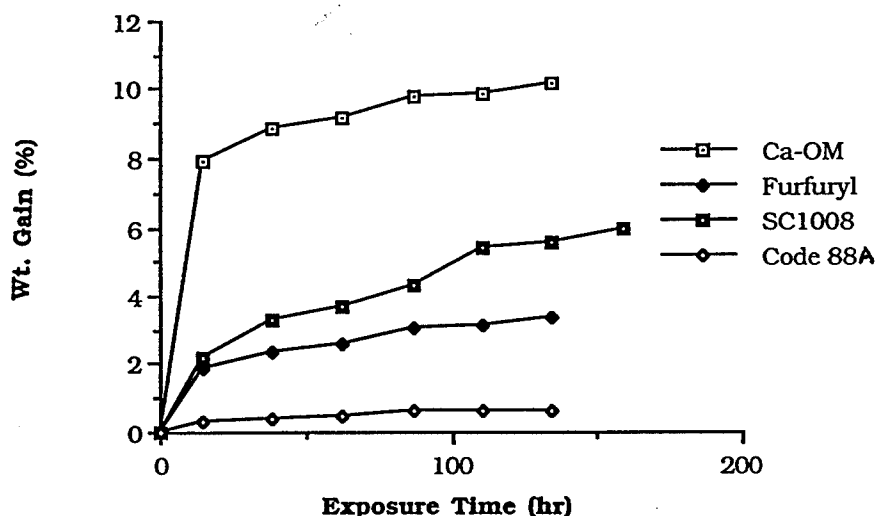


**Figure 9. Hydrolysis Reaction at Oxygen Bridges**

As shown in Table 3, Code88A char has a much lower percentage of  $B_2O_3$  as compared to the rest of the samples. This explains the relatively low moisture affinity of Code 88A char. As the sample oxidizes, the boron sub-oxides will eventually turn into  $B_2O_3$ , and the moisture resistivity of this sample may disappear.

The moisture resistance of the carbon chars after oxidation was also monitored. Figure 10 shows the results. Again, the calcium organometallic compound added carbon foam (Ca-OM) showed a significant amount of moisture pick-up due to its large surface area. The Code88A sample showed less moisture affinity than the standard 5% carborane added SC1008. Weight gains of the oxidized samples were

much higher than the pre-oxidation results. This is attributed to the much higher  $B_2O_3$  content of the oxidized samples. All samples, except Code88A char, appeared gray after air exposure. Hydrolysis of  $B_2O_3$  yields a white powdery hydroxide on the carbon surface. The Code88A liquid pitch system showed the most promise in moisture resistance. Consequently, this system was chosen for composite impregnations.



**Figure 10. Moisture Adsorption of Carbon Chars after Oxidation**

### 2.2.3 TGA Study

Thermogravimetric analysis (TGA) was also used to characterize the oxidation resistance of the carbons. The as-cured resins were cut into small pieces and sent to Kaiser Aerotech, a well known manufacturer of carbon-carbon composites, for analysis. Each sample was carbonized in an inert atmosphere to 900°C at a heating rate of 10°C/min. After cooling down to room temperature, the samples were oxidized in flowing air under a similar thermal ramp. The weight loss vs. temperature curves of the carbonization and oxidation process are shown in Figures 11 to 19. Char yield and oxidation rate of the carbon precursors from TGA runs are not quantitative, as they are strongly dependant on the sample size (or surface area per unit weight). However, the temperature of weight loss onset during carbonization and oxidation will not be affected by the sample size.

Carbonization of the SC1008 phenolic resin showed three main weight losses (rates of >1.0%/min.) at temperatures of 325, 460 and 600°C (Figure 11). With carborane additions, a wide band of weight loss at less than 500°C and a sharp weight loss at 670°C was observed (Figure 12). Oxidation of the SC1008 sample showed that the reaction started at about 600°C and the sample was completely oxidized before 900°C. For the 5% carborane/SC1008 samples, an additional weight loss at 200°C of about 0.25%/min. was observed. At about 650°C, the carborane added char started to oxidize and a reduction in the rate of weight loss was noted (Figure 13).

TGA File Name: pc1  
 Sample Weight: 25.400 mg  
 Fri Sep 06 10:53:02 1991  
 cured phenolic resin.

PERKIN-ELMER  
 7 Series Thermal Analysis System  
 N<sub>2</sub>

TGA 1st Derivative: pc1  
 Sample Weight: 25.400 mg  
 Fri Sep 06 10:53:02 1991  
 cured phenolic resin.

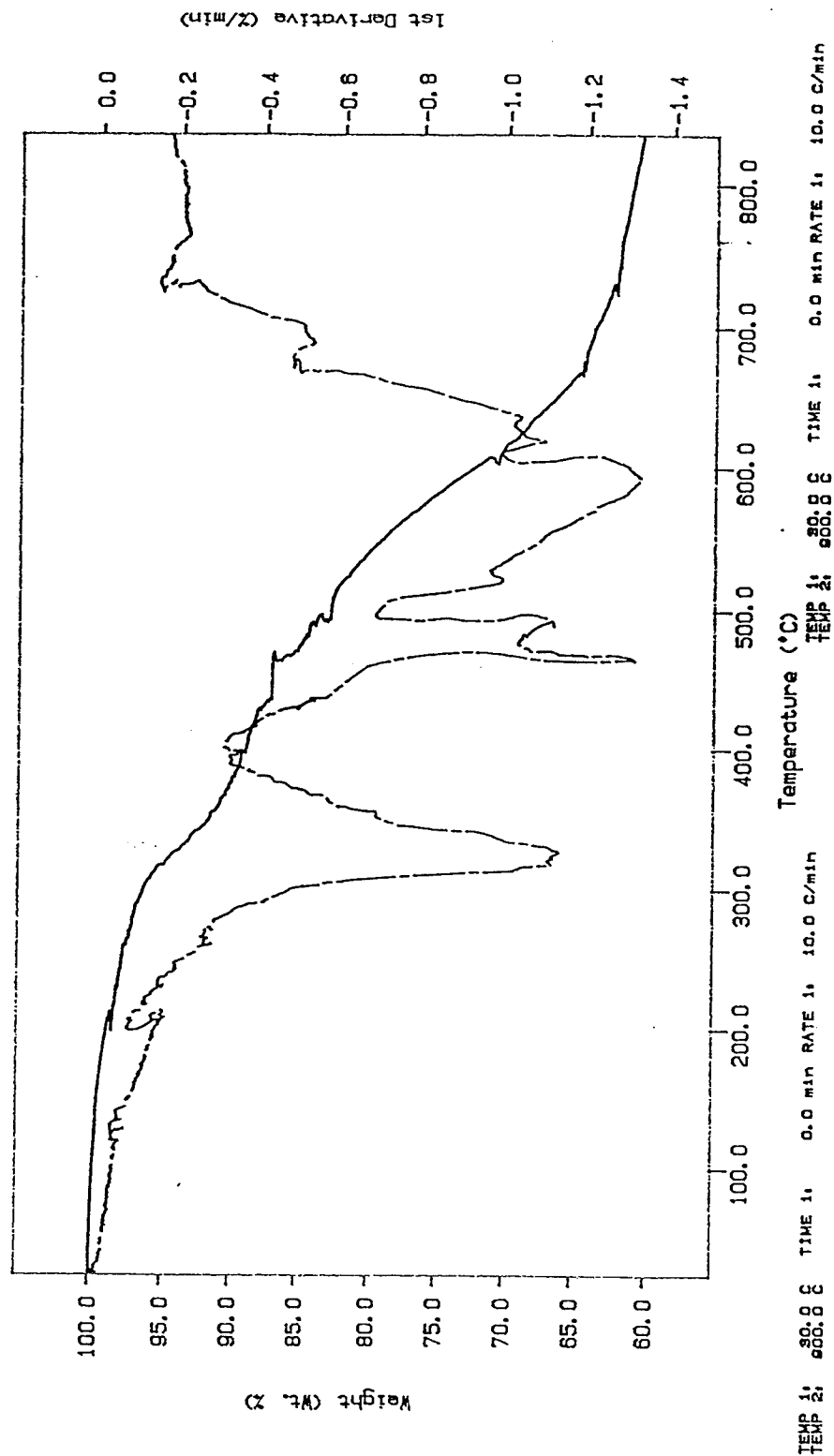


Figure 11. TGA Results, Carbonization of SC1008

TGA File Name: phil12  
 Sample Weight: 29.848 mg  
 Fri Sep 08 15:38:38 1991  
 5% o-carborane -  
 in nitrogen  
 PERKIN-ELMER  
 7 Series Thermal Analysis System

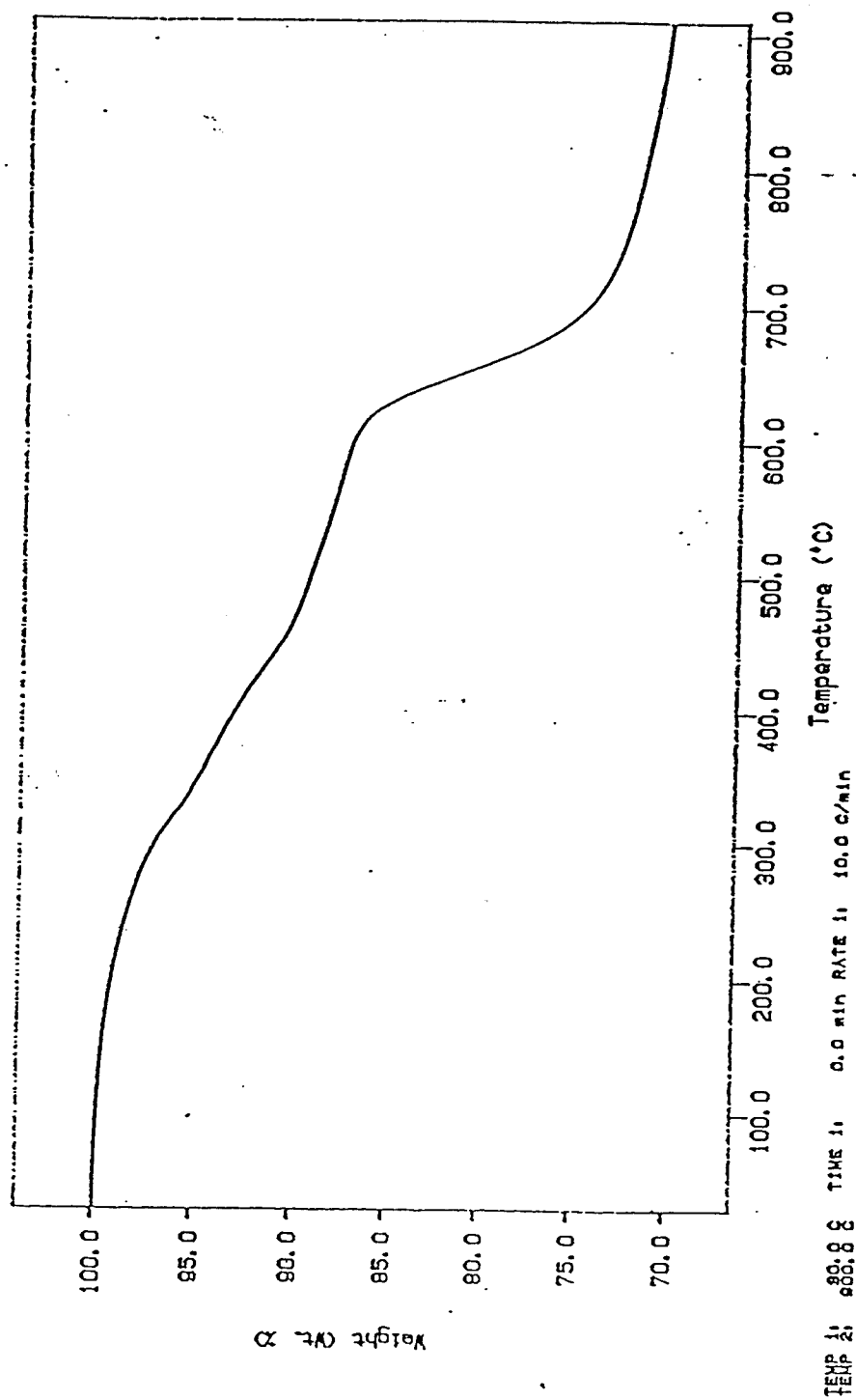


Figure 12. TGA Results, Carbonization of 5% Carborane Added SC1008

TGA File Name: po2a  
 Sample Weight: 22.832 mg  
 Thu Sep 12 11:38:48 1991  
 5% O-Carborane, after carb, in air

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: po2a  
 Sample Weight: 22.832 mg  
 Thu Sep 12 11:38:48 1991  
 5% O-Carborane, after carb, in air

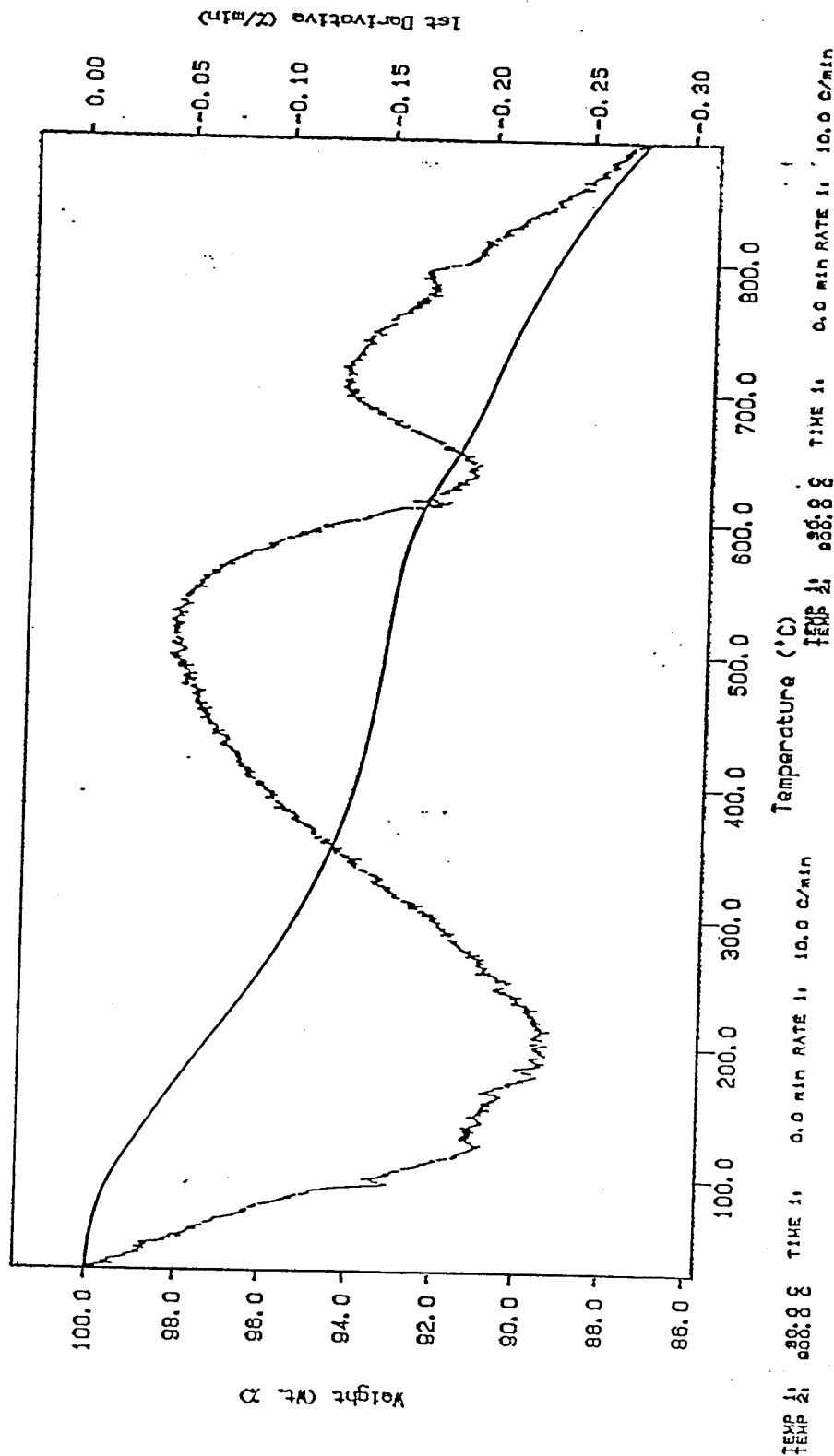


Figure 13. TGA Results, Oxidation of 5% Carborane Added SC1008 Char



Considering that this carborane added char had been carbonized at 900°C and that the SC1008 phenolic char did not show oxidation at temperatures less than 600°C, this low temperature loss must be attributed to the added boron. Glasses high in B<sub>2</sub>O<sub>3</sub> degrade by hydrolysis under ambient conditions. Hydrolysis results in the formation of orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) at low temperature.<sup>3</sup> Heating H<sub>3</sub>BO<sub>3</sub> above 100°C results in the release of water vapor and the formation of metaboric acid (HBO<sub>2</sub>). Above 250°C, HBO<sub>2</sub> begins to transform to B<sub>2</sub>O<sub>3</sub> with the release of water vapor.

To minimize the effects of moisture absorption on TGA oxidation data, the furfuryl and Code88A samples were analyzed *in-situ* immediately following carbonization in the TGA set-up. The carborane added furfuryl sample showed different weight loss patterns during the carbonization and oxidation runs from those of carborane added phenolic. Weight loss of the carbonization process mainly occurs at 400°C, about 250°C lower than that of phenolic samples. The onset temperature of oxidation for furfuryl sample is also about 50°C lower than that of phenolic (Figures 14 and 15).

Carbonization of the Code88A sample shows a very different weight loss pattern than that of the phenolic sample. Weight loss of the Code88A liquid pitch mainly occurs at temperatures below 300°C (Figure 16). Oxidation of the Code88A char shows similar weight loss pattern as that of the phenolic char, i.e., weight loss onset at ~600°C (Figure 17). Addition of carborane did not significantly affect the weight loss patterns of the Code88A sample during TGA carbonization and oxidation runs (Figures 18 and 19).

### 2.3. Composite Fabrication Process

Two types of carbon-carbon composites were fabricated in this program: baseline and inhibited systems. Both composites were reinforced with AMOCO's 3K, T-300 PAN fiber in an 8 Harness Satin weave with 24x23 end counts. The fabrics were heat stabilized to 2482°C (4500°F) by Fiberite to reduce shrinkage during the subsequent carbon-carbon processing.

The baseline carbon-carbon composites contained a K-641 phenolic resin in the prepreg matrix and were densified with Kaiser's proprietary liquid pitch, Code88A. The prepreg matrix precursor for the inhibited carbon-carbon composite contained a mixture of K-641 phenolic resin and 5 wt% of *o*-carborane. A mixture of Code88A with 5 wt% of *o*-carborane was used in the densification processes to increase the carborane content in the inhibited composites.

#### 2.3.1 Prepreg Preparation

PAN based carbon fiber fabric was used to fabricate the prepreps for inhibited composites at Fiberite. Five wt% *o*-carborane added SC1008 phenolic resin was prepared and used for the preprepping operation. No calcium was added in the phenolic resin as none of the calcium organometallic provided moisture resistance. (See Sec. 2.1.2) Only the inhibited system was preprepped in this program. The baseline prepreg, with standard K-641 phenolic resin (SC1008), was transferred from another program.

TGA File Name: bfur3  
 Sample Weight: 14.970 mg  
 Wed Aug 07 12:06:43 1996  
 5% carborane in furfuryl (317-07)

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: bfur3  
 Sample Weight: 14.970 mg  
 Wed Aug 07 12:06:43 1996  
 5% carborane in furfuryl (317-07)

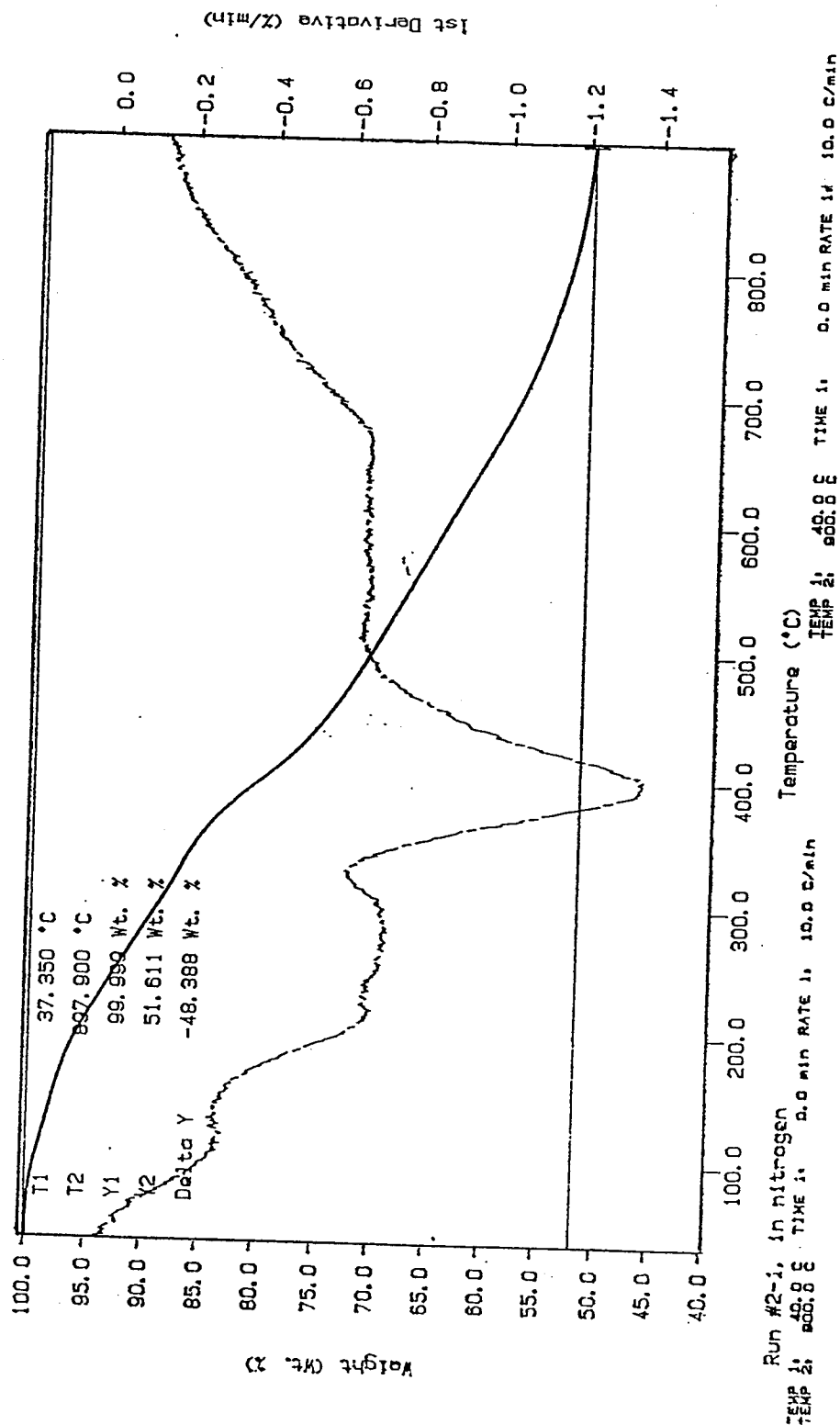


Figure 14. TGA Results, Carbonization of 5% Carborane Added Furfuryl

TGA File Name: bfur6  
 Sample Weight: 7.132 mg  
 Fri Aug 09 19:39:22 1998  
 5% carborane in furfuryl (317-07)

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: bfur6  
 Sample Weight: 7.132 mg  
 Fri Aug 09 19:39:22 1998  
 5% carborane in furfuryl (317-07)

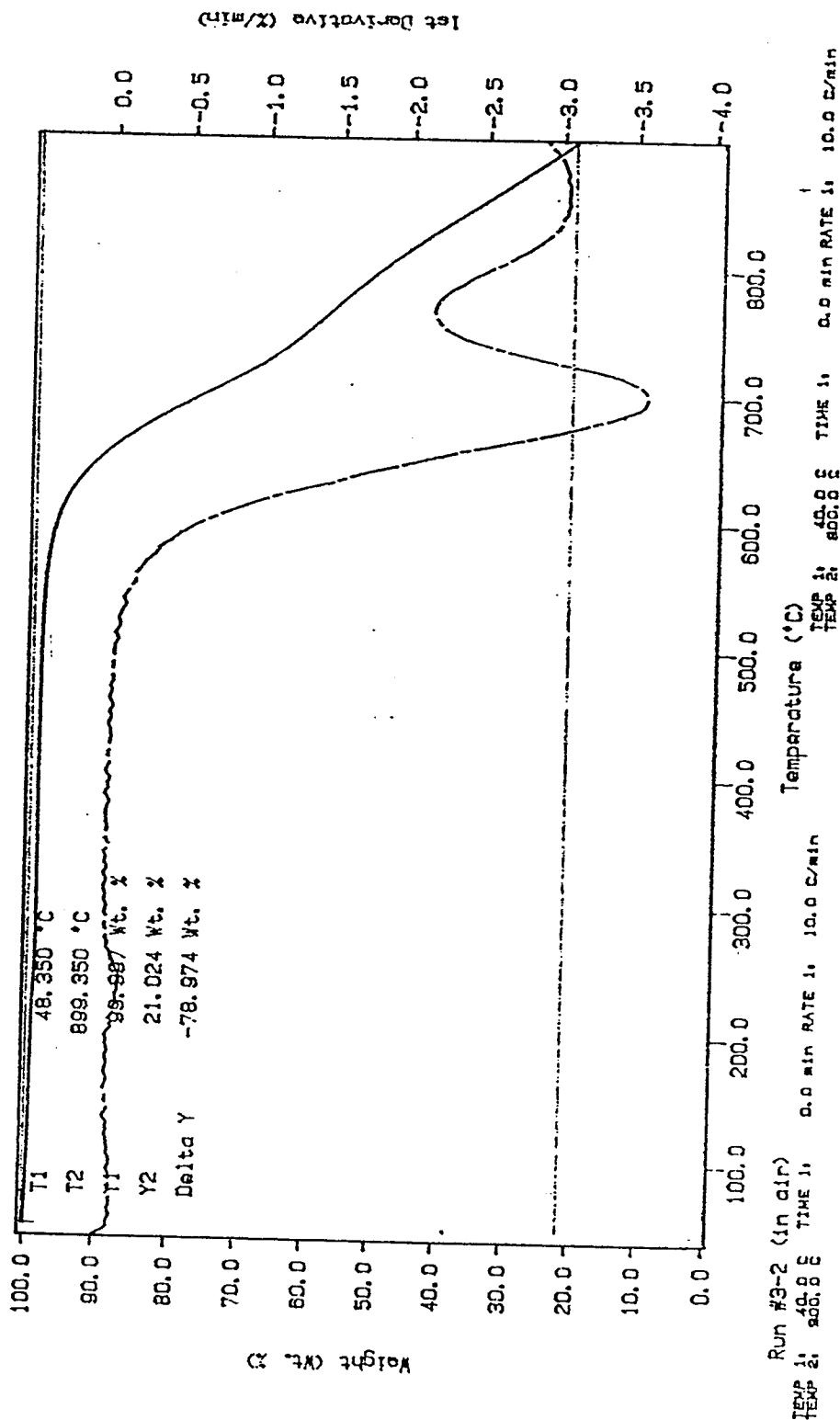


Figure 15. TGA Results, Oxidation of 5% Carborane Added Furfuryl Char

TGA File Name: carb  
 Sample Weight: 18.965 mg  
 Fri Jan 22 12:31:07 1993  
 code 88 (as-dried)

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative carb  
 Sample Weight: 18.965 mg  
 Fri Jan 22 12:31:07 1993  
 code 88 (as-dried)

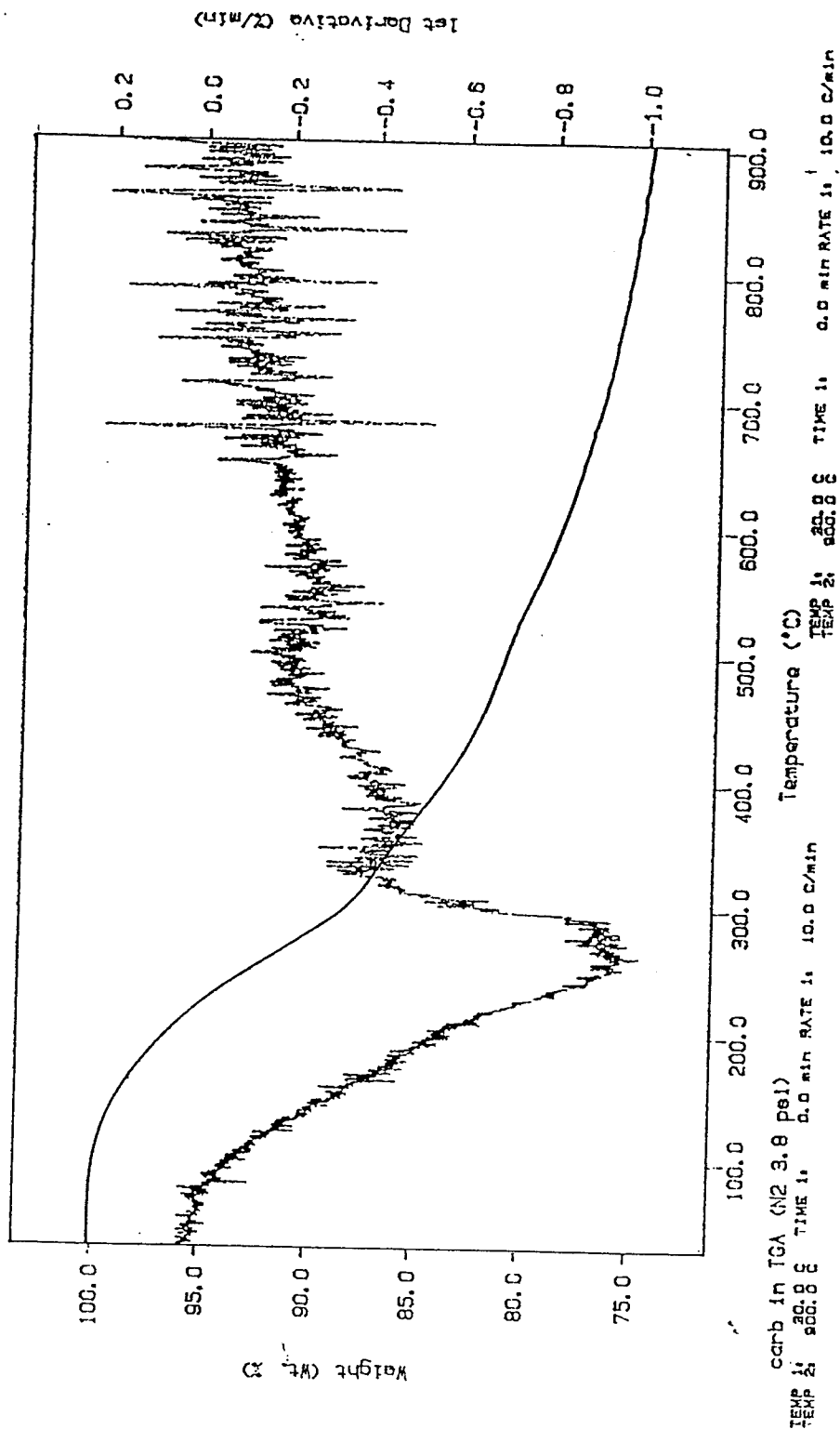


Figure 16. TGA Results, Carbonization of Code 88

TGA File Name: car4  
 Sample Weight: 17.545 mg  
 Sun Jan 17 14:39:05 1993  
 Carbonized code 88

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: car4  
 Sample Weight: 17.545 mg  
 Sun Jan 17 14:39:05 1993  
 Carbonized code 88

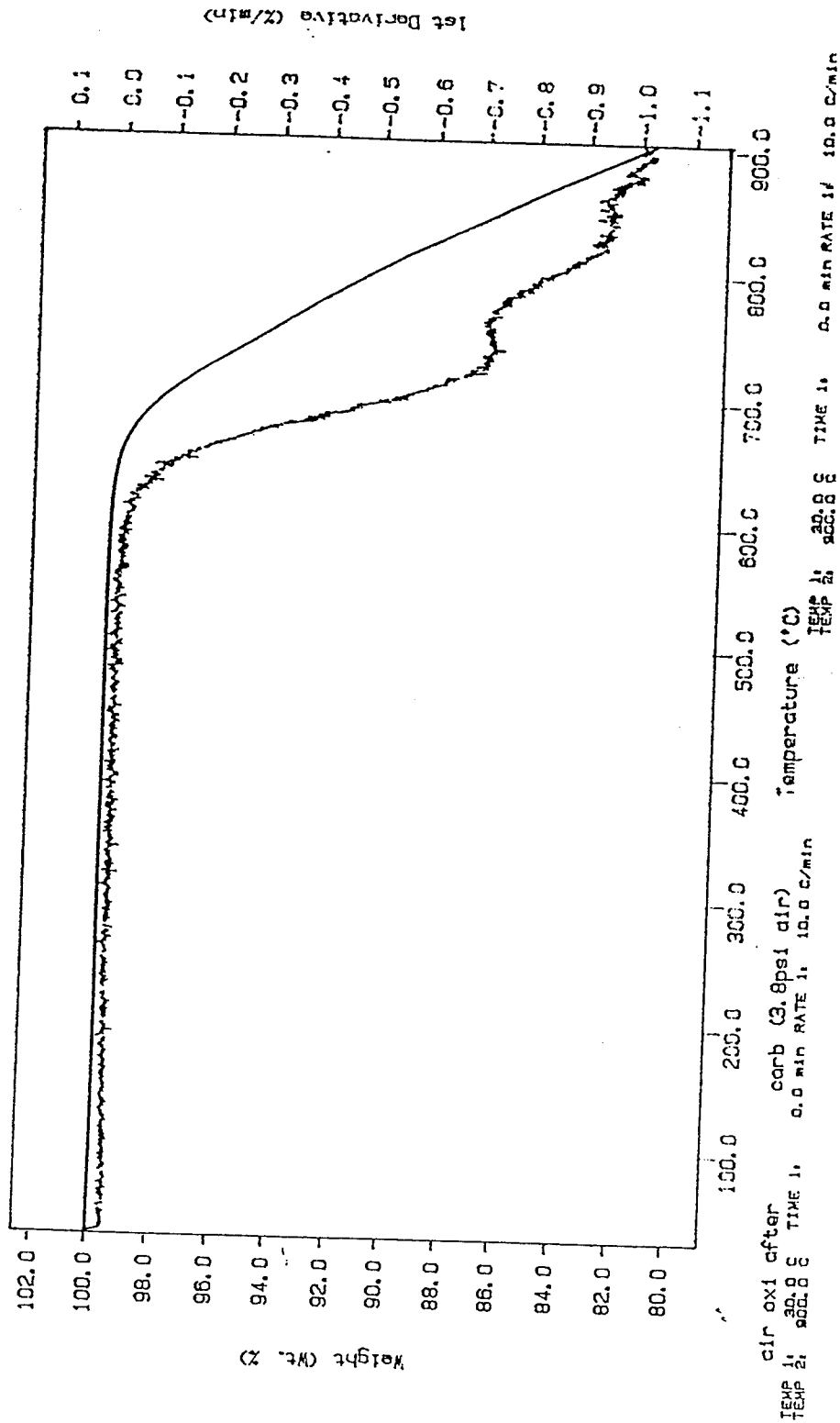


Figure 17. TGA Results, Oxidation of Code 88 Char

TGA File Name: car6  
 Sample Weight: 18.362 mg  
 Mon Jan 18 13:01:34 1993  
 Cured code 88 + carborane

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: car6  
 Sample Weight: 18.362 mg  
 Mon Jan 18 13:01:34 1993  
 Cured code 88 + carborane

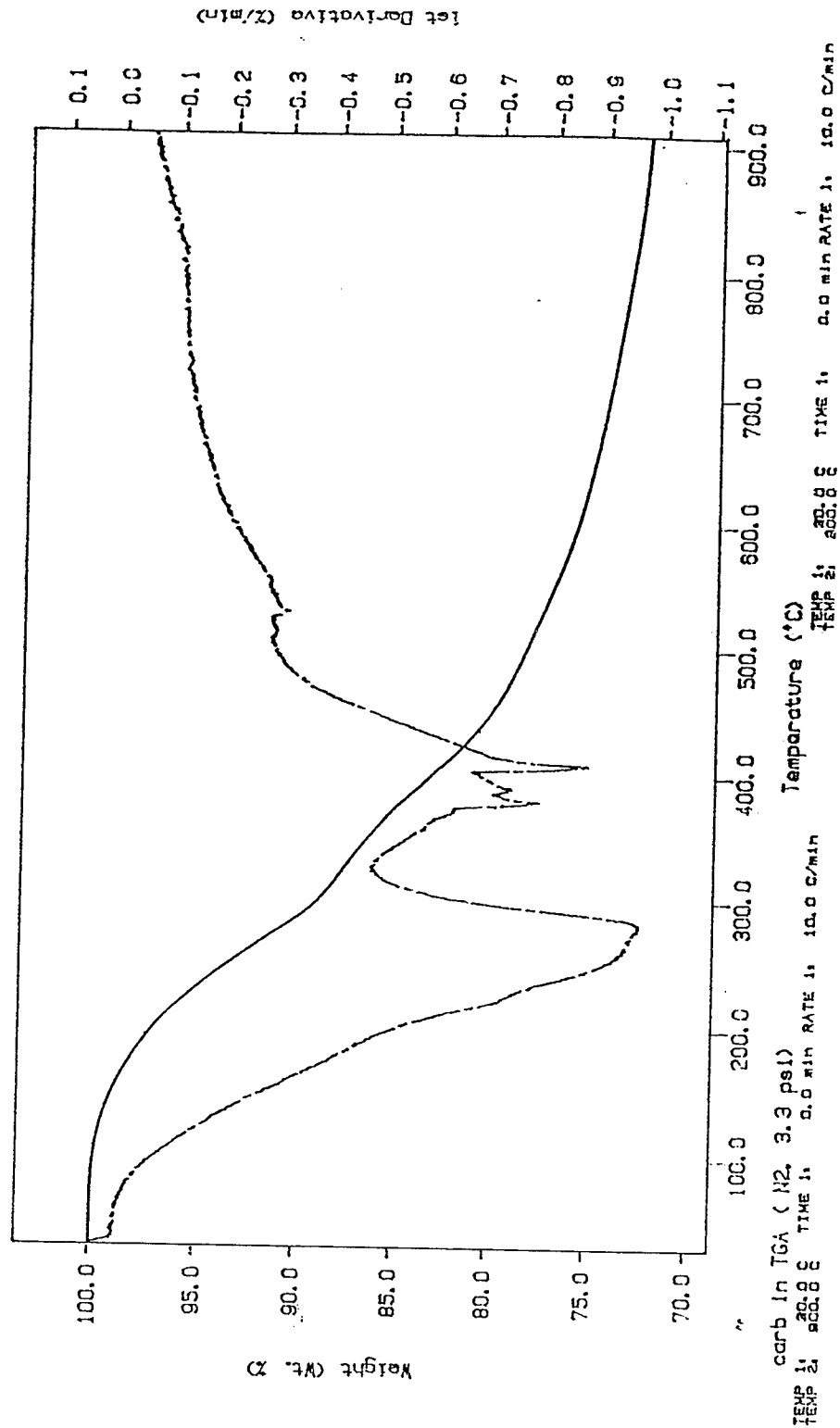


Figure 18. TGA Results, Carbonization of 5% Carborane Added Code 88

TGA File Name: car7  
 Sample Weight: 13.365 mg  
 Mon Jan 18 15:31:55 1993  
 Carbonized code 88 + carborane

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: car7  
 Sample Weight: 13.365 mg  
 Mon Jan 18 15:31:55 1993  
 Carbonized code 88 + carborane (2)

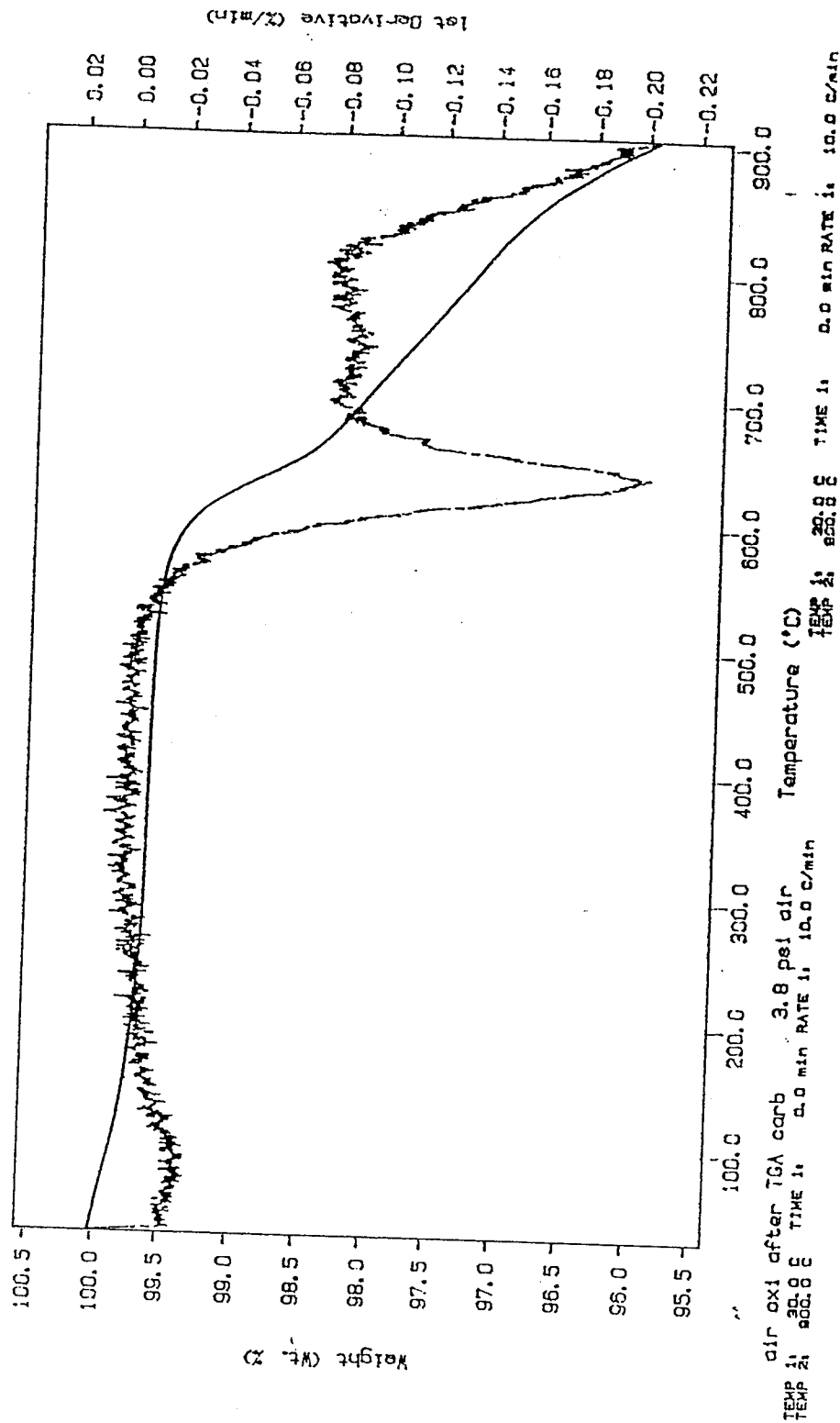


Figure 19. TGA Results, Oxidation of 5% Carborane Added Code 88 Char

A solution method was used for the prepreg preparation. The fabric was first immersed in a dip pan which contained the freshly mixed resin, then pulled through a pair of rollers. The gap between the rollers was adjusted to control the resin content of the prepreg. After the rolling process, the prepreg passed through an air circulating oven to remove excess volatile. Volatile content of the prepreg was controlled by prepreg take-up speed and oven temperature.

Two different batches of prepreg, with the same fiber reinforcement and resin, were used for the fabrication of baseline panels. The properties of both batches of prepreg are summarized in Table 5. The second batch prepreg has an unexpected higher flow. As shown in Table 5, the flow of this sample was adjusted, through staging at 77°C (170°F), to be similar to the flow and volatile content of the first batch.

Table 5 also shows the properties of the carborane added prepreg. Again, staging (170°F, 100 minutes in an air circulating oven) was used to modify the flow and volatile% of the prepreg. Figure 20 shows the TGA weight loss pattern of the inhibited prepreps, before and after staging. Staging mainly reduces the amount of volatile. The staged inhibited prepreg has similar flow and volatile% as that of baseline materials. Figure 21 shows the TGA weight loss patterns of fresh inhibited and K641 prepreps. The inhibited prepreg showed less weight loss at temperatures between 400 and 600°C.

**Table 5.  
Properties of the Prepreps**

Material	Test	Flow at 200 psi (%)	Resin Solids (%)	Volatile (%)
Inhibited Prepreg	Fiberite	19.4	33	5.4
	KA	20	N/A	5.2
Baseline Prepreg (1)	Fiberite	20	33	4 - 7
	KA	12.8*	N/A	4.2
Baseline Prepreg (2)	Fiberite	25.3	34	5.6
	KA	25.8	36	5.0
KA Requirement		17 - 20	30 - 36	4 - 7

\* After 1 hour staging at 175°F



TGA File Name: atm  
 Sample Weight: 8.448 mg  
 Thu Sep 19 14:45:30 1996  
 ATM Prepreg

# PERKIN-ELMER 7 Series Thermal Analysis System

TGA File Name: atm1  
 Sample Weight: 8.993 mg  
 Thu Sep 19 13:27:45 1996  
 ATM Prepreg, 1 hr staged at 170F

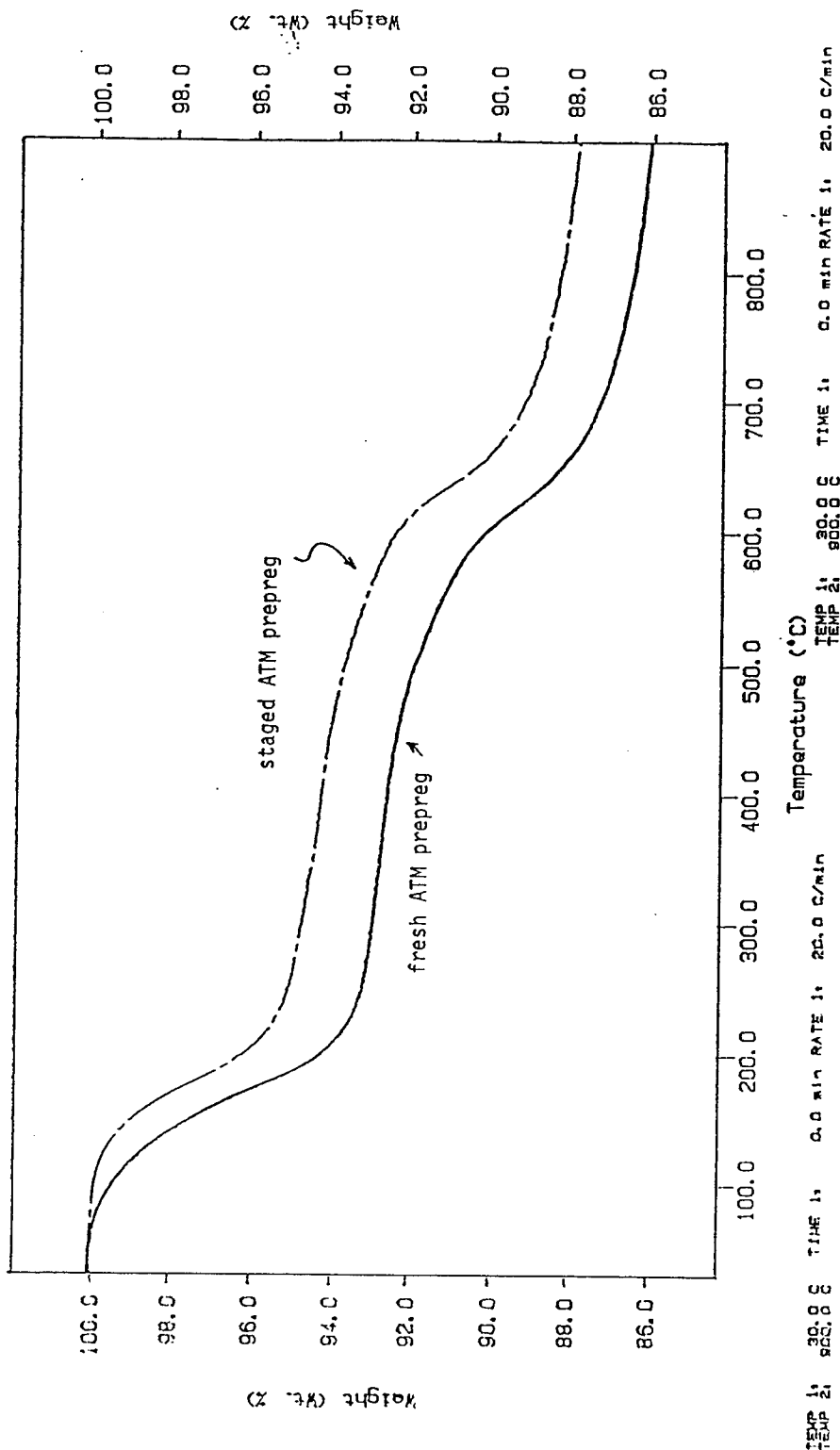


Figure 20. TGA Weight Loss Patterns of the Inhibited Prepregs, Before and After Staging

TGA File Name: K641  
 Sample Weight: 9.026 mg  
 Thu Sep 19 16:15:09 1996  
 K641 Prepreg

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA File Name: atm  
 Sample Weight: 8.448 mg  
 Thu Sep 19 14:45:30 1996  
 ATM Prepreg

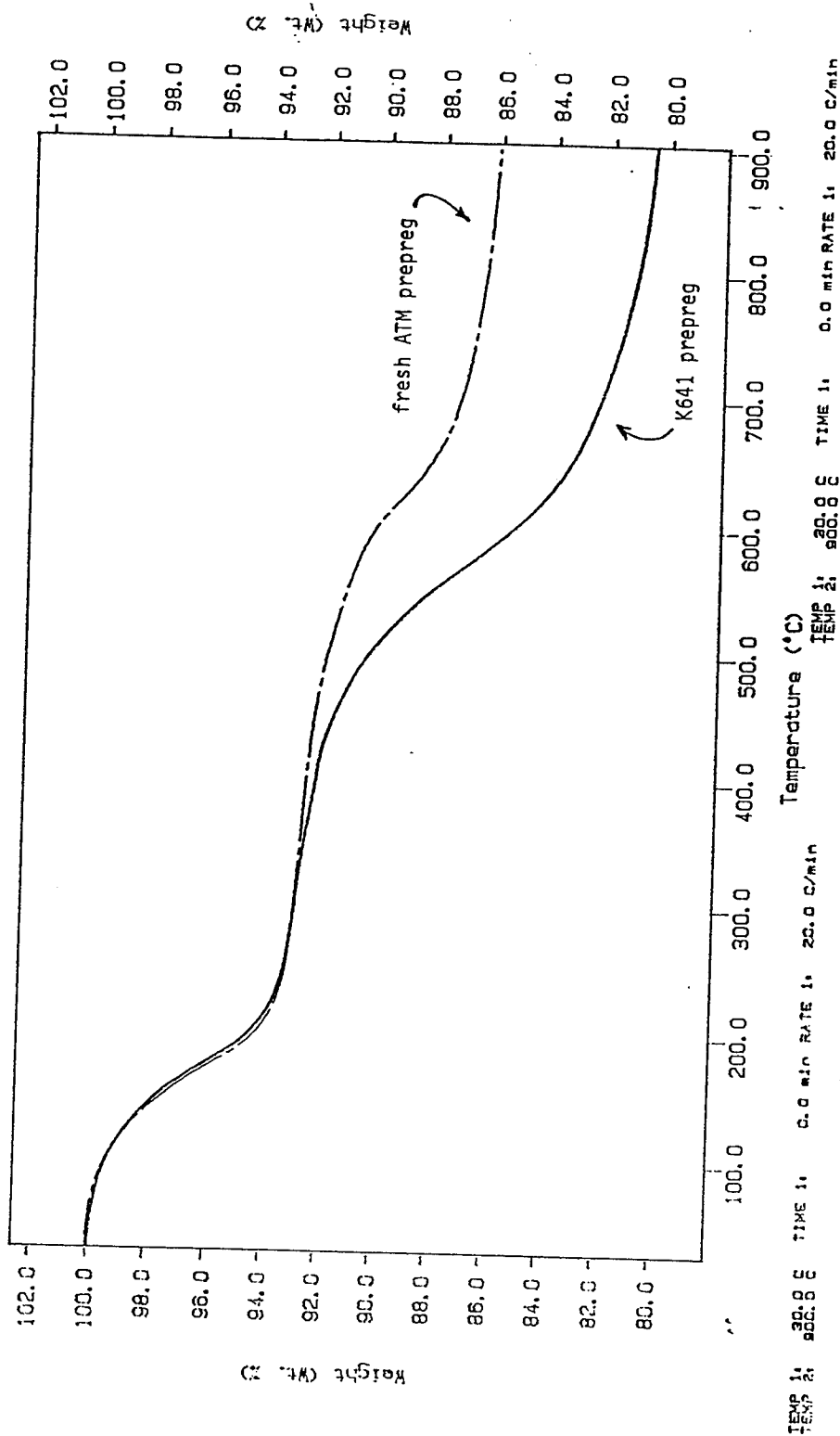


Figure 21. TGA Weight Loss Patterns of Fresh K641 and Inhibited Prepregs

### 2.3.2 Cure

Differential Scanning Calorimetry (DSC) was used to characterize the baseline and inhibited prepregs. DSC detected the amount of heat generated during the cure process. By comparing the exotherms between the baseline and inhibited prepregs, the curing rate can be modified appropriately.

Figures 22 and 23 show the DSC results of the baseline and inhibited prepreg. Prepregs were tested between 50 and 300°C with a heating rate of 20°C/min. After the DSC run (designated as 1st run), the cured sample was then used to establish the baseline (2nd run). The subtracted curves of the baseline and inhibited prepregs did not show much difference. The onset of exothermic reaction in the inhibited system started at a lower temperature than the baseline material, indicating a need for good temperature control at the early stage of the cure process.

A small panel, 4" x 4" x 6 plies, was prepared in a hot press under vacuum bag set-up to check the feasibility of the processing of inhibited prepreg. The ply thickness of the as-cured panel was calculated to be ~11.5 mils, within the range of baseline material. The 4" x 4" panel was then carbonized with a fast heating cycle. The carbonized panel had excellent integrity with a ply thickness of 11.2 mils.

Both the baseline and inhibited prepregs were cut into 11" warp x 10" fill plies. They were staged and vacuum bag cured in an autoclave. All the inhibited panels which were cured in the autoclave delaminated, while all the baseline panels passed the x-ray inspection. The heating rate of the autoclave in the initial heat up was much slower than the press due to the poor heat transfer. This low initial heating rate may be responsible for the panel delamination as the skin of the panel may cure before the center of the panel. To prevent the delamination, all the inhibited panels were prepared and cured in the press, and panels all passed the x-ray inspection.

### 2.3.3 Carbonization and Densification

The first carbonization cycle, conversion of cured prepreg resin to carbon, is considered the most critical step in the carbon-carbon composite process. To ensure a successful carbonization process, staged and cured composite samples (both baselines and inhibited) were analyzed by TGA during carbonization under N<sub>2</sub> to determine the appropriate heating cycle.

#### 2.3.3.1 TGA Test

Figures 24 and 25 show the TGA test results of cured baseline and inhibited samples. Both materials showed a small weight loss of 1-2% below 200°C. This initial weight loss was attributed to the evolution of water, a reaction byproduct. A significant amount of weight loss occurred above 400°C for both samples due to matrix decomposition. The inhibited sample showed a slightly higher yield, similar to the results of prepreg carbonization. Due to this lower weight loss, the inhibited panels were successfully carbonized using the standard carbonization cycle. Although both the baselines and inhibited composite panels survived the first carbonization cycle as indicated by the x-ray inspection, one of the inhibited panels showed signs of low density.

DSC Subtraction  
 Sample Weight: 22.050 mg  
 Tue Sep 24 13:40:07 1996  
 K641 Prepreg  
 (Subtracted)

PERKIN-ELMER  
 7 Series Thermal Analysis System

DSC Data File: K6411  
 Sample Weight: 22.050 mg  
 Tue Sep 24 13:40:47 1996  
 K641 Prepreg

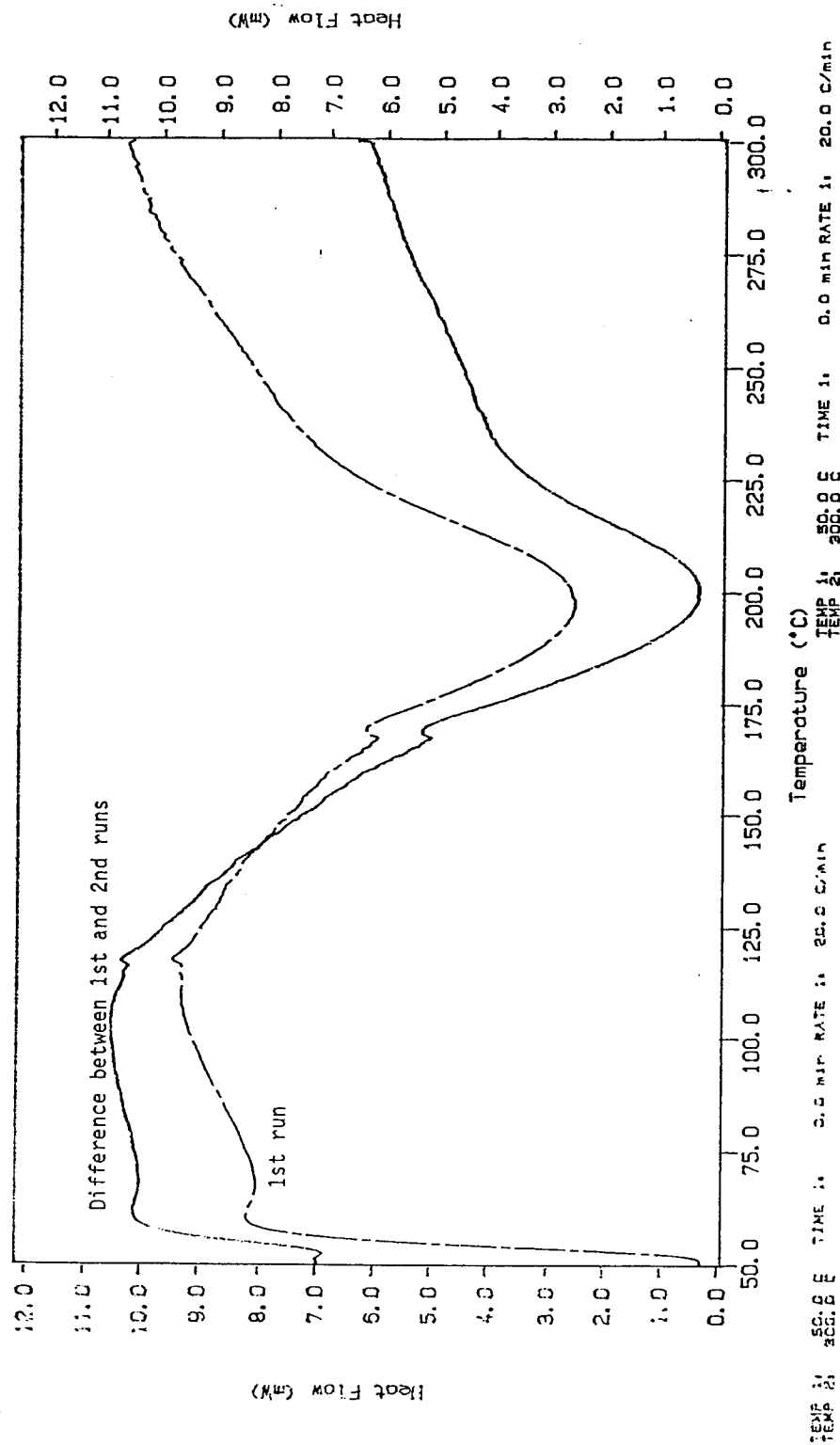


Figure 22. DSC Results of Baseline Prepreg

DSC Subtraction  
 Sample Weight: 18.350 mg  
 Tue Sep 24 14:42:18 1996  
 ATM Prepreg  
 (Subtracted)

PERKIN-ELMER  
 7 Series Thermal Analysis System

DSC Data File: csm2  
 Sample Weight: 18.350 mg  
 Tue Sep 24 14:42:18 1996  
 ATM Prepreg

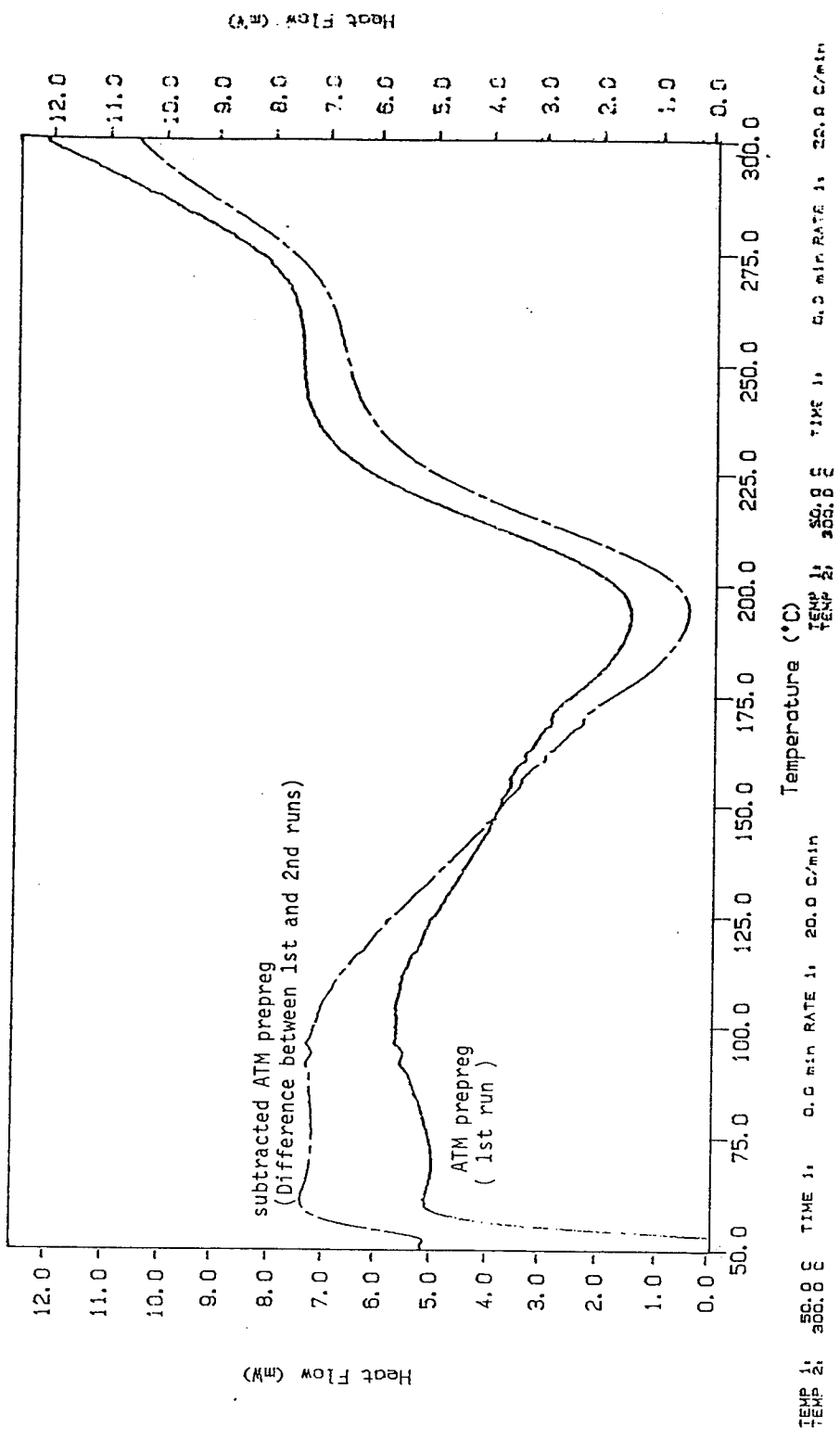


Figure 23. DSC Results of Inhibited Prepreg

TGA File Name: K6413  
 Sample Weight: 26.274 mg  
 Wed Oct 23 18:01:43 1996  
 K641 101-1B, as-cured (TGA Carb)

**PERKIN-ELMER**  
**7 Series Thermal Analysis System**

TGA lot Derivative: K6413  
 Sample Weight: 26.274 mg  
 Wed Oct 23 18:01:43 1996  
 K641 101-1B, as-cured (TGA Carb)

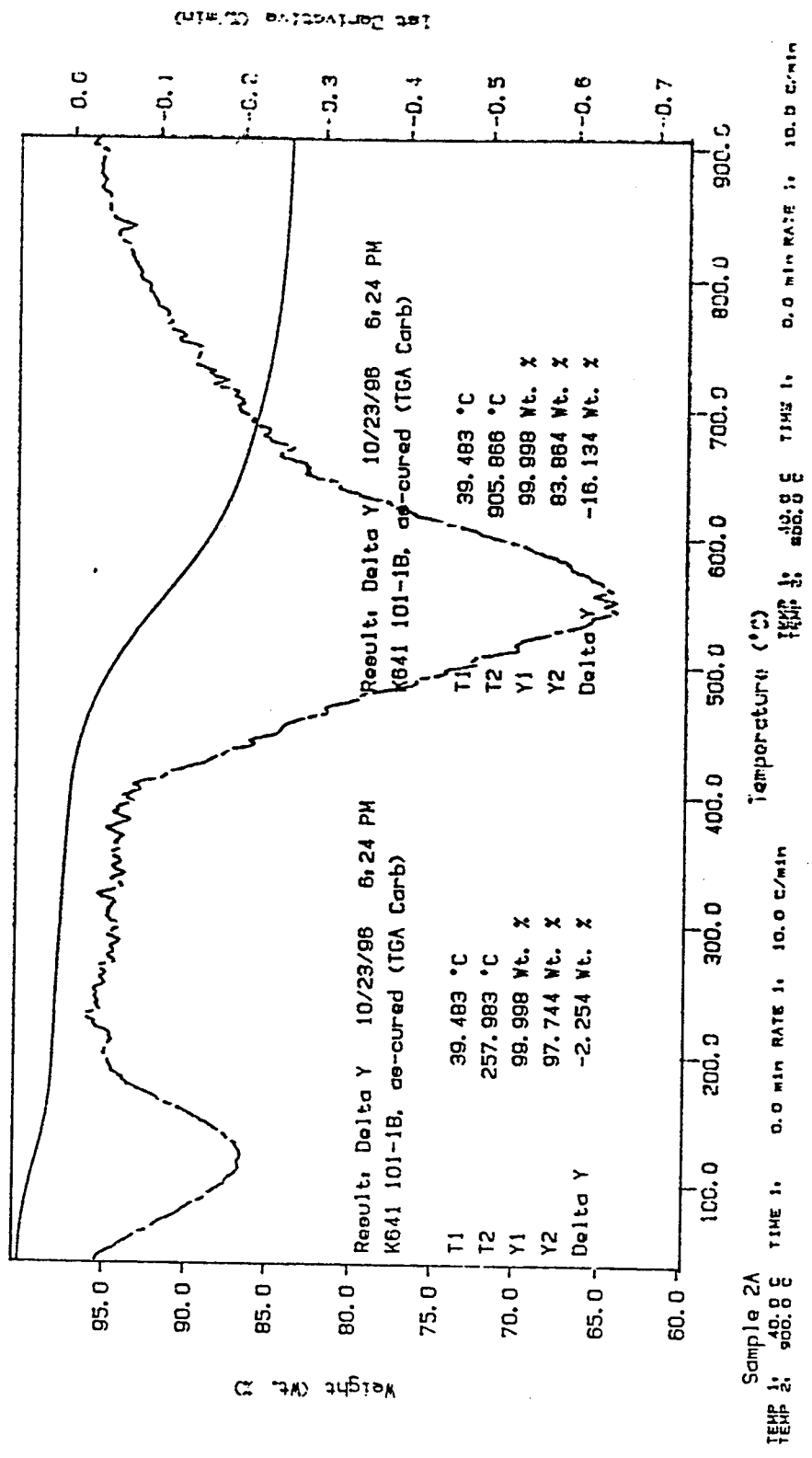


Figure 24. TGA Results of Cured Baseline System

TGA File Name: bor7  
 Sample Weight: 14.617 mg  
 Tue Nov 26 14:22:43 1998  
 ATM-6 (as-cured) sample 4

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: bor7  
 Sample Weight: 14.617 mg  
 Tue Nov 26 14:22:43 1998  
 ATM-6 (as-cured) sample 4

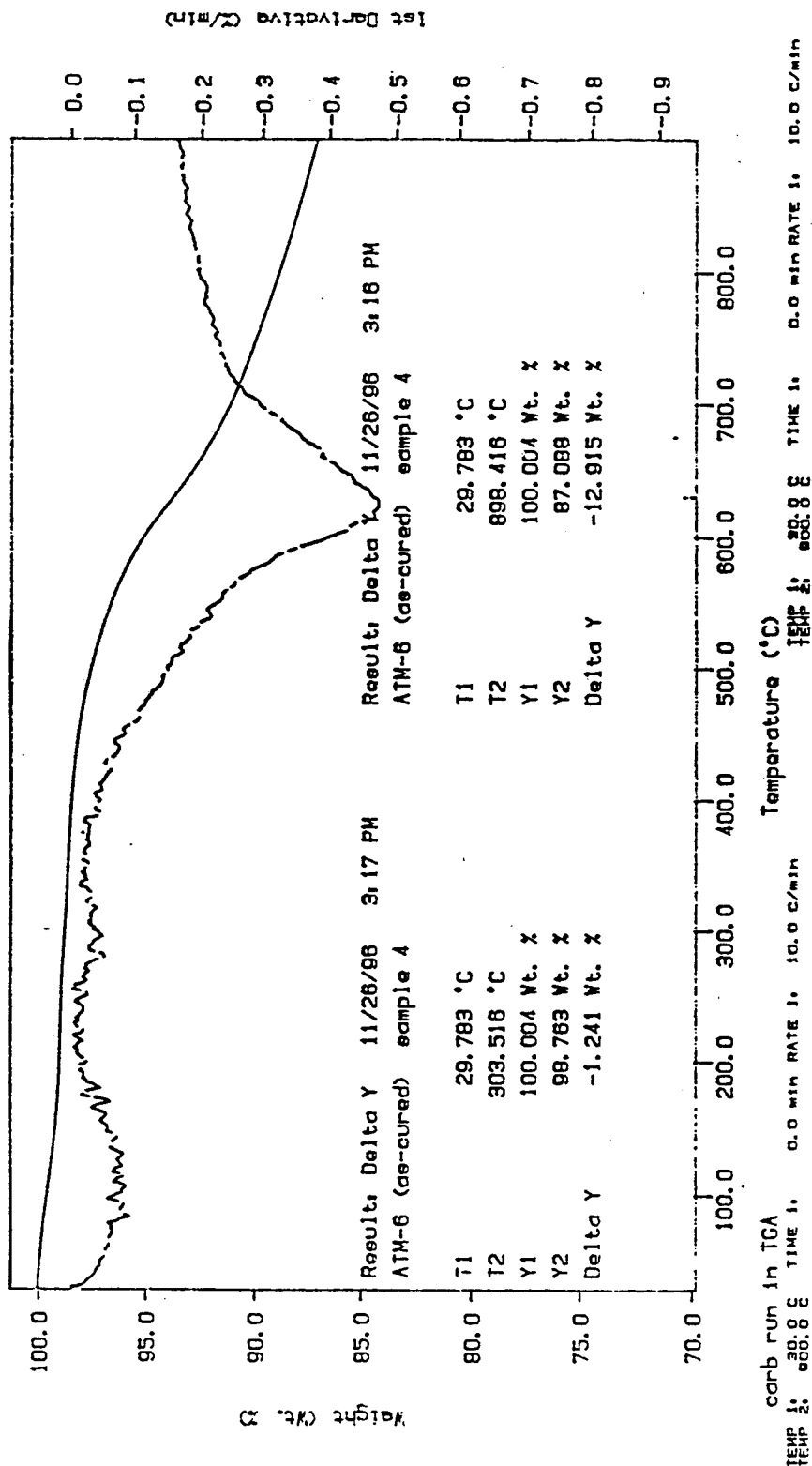


Figure 25. TGA Results of Cured Inhibited Samples

### 2.3.3.2 Densification Process

Kaiser Code88A liquid pitch, with a viscosity of 30 to 100 cps, was used to densify the baseline panels. In order to conserve the carborane chemical, the inhibited composite panels were cut into small panels (5"x7") for impregnations in a small vessel with carborane-added Code88A. After the final carbonization, significant amounts of local delamination (and low density) were detected in some of the inhibited panels by x-ray inspection.

### 2.3.3.3 Composite Heat Treatment

Both the baseline and inhibited composites were heat-treated to 1427°C (2600°F) at Union Carbide to stabilize the matrix material to the application temperatures. To prevent further delamination, all the inhibited panels were machined to small coupons prior to the heat treatment. All the inhibited samples passed the x-ray inspection after the high temperature heat treatment.

Vaporization of boron oxide in the form of  $\text{BO}_x$ ,  $x = 2$  or  $3$ , becomes significant at elevated temperatures. Some of the carborane inhibitor was oxidized into boron oxide,  $\text{B}_2\text{O}_3$ , during the cure and densification processes.  $\text{B}_2\text{O}_3$  can further react into  $\text{BO}_2$  or  $\text{BO}_3$  vapors during the high temperature heat treatment. The loss of boron oxide through vaporization can affect the oxidation resistance of the composites.

### 2.3.3.4 The fourth Densification Cycle

Table 6 lists the density and open porosity of the carbon-carbon composites. Both the baseline and inhibited sample have a density less than the  $1.70 \text{ g/cm}^3$  target after the 1427°C (2600°F) heat treatment. This low density is attributed to the lack of a normal 2482°C (4500°F) graphitization process. In a standard carbon-carbon process, samples are graphitized after the first carbonization to open up the porosity. Without this critical porosity opening process, the efficiency of densification and the density of the composite are compromised. The significantly lower density, and higher porosity content, in the inhibited samples indicates the loss of matrix inhibitor through the vaporization of boron oxide.

Since the mechanical properties of carbon-carbon composites depend strongly on their densities, both the baseline and inhibited composites used for mechanical testing were subjected to a fourth densification. The density of the inhibited samples increased significantly (~5%) after the fourth densification. This dramatic improvement in density is attributed to the porosity opening, through matrix shrinkage and boron loss, from the 2600°F heat treatment.

## 2.4 Composite Characterization

### 2.4.1 Distribution and Compositional State of Boron

The boron state of the modified composite matrix, before and after oxidation, was determined by ESCA. ESCA study of the composite matrix is much more complicated as there are two carbon chars, the Code88A and phenolic, in the matrix. Composite cross-section, with perpendicular and parallel fiber areas, was used for ESCA analysis. The perpendicular fiber areas, i.e., fiber bundles with primarily a



phenolic resin char from the prepreg, were examined with a 200 $\mu$ m spot size (the composite has a ply thickness of ~300 $\mu$ m). On the other hand, the parallel fiber areas were examined with a spot size of 600  $\mu$ m to maximize the coverage of the between-ply area, which is composed of mainly Code88A char.

**Table 6**  
**Density and Open Porosity of Carbon-Carbon Composites**

<u>Material</u>	<u>Process</u>	<u>Bulk Density</u> (g/cm <sup>3</sup> )	<u>Wet Density</u> (g/cm <sup>3</sup> )	<u>Open Porosity</u> (%)
Baseline C-C	2600°F HT	1.68	1.74	3.8
	4 Densifications	1.70	1.73	1.8
Inhibited C-C	2600°F HT	1.65	1.83	9.8
	4 Densifications	1.73	1.79	3.6

The atomic concentration results of the composite matrix are summarized in Table 7. The parallel fiber area, with Code88A char, contained slightly more boron than the perpendicular area. This is consistent with the higher boron content of Code88A char as shown in Table 1. As expected, the post-oxidized samples (600°C, 1 hour in air) showed a higher concentration of boron and oxygen than the pre-oxidized samples.

**Table 7. Atomic Concentration of Elements Detected**

<u>Sample</u>	<u>Acq. Type</u>	<u>Size(<math>\mu</math>m)</u>	<u>O</u>	<u>C</u>	<u>B</u>
Pre-oxidized, parallel	Med. Res.	600	9.4	88.6	2.0
Pre-oxidized, perpend.	Med. Res.	200	8.6	90.1	1.2
Post-oxidized, parallel	Med. Res.	600	10.8	86.2	3.0
Post-oxidized, perpend.	Med. Res.	200	8.6	88.8	2.6

The poor signal-to-noise ratios of the parallel fiber data made curve fitting less certain than before, and the data from the perpendicular fibers was too poor to curve fit. The majority of the B 1s peak lies at energy of 192.6 eV where B<sub>2</sub>O<sub>3</sub> or H<sub>3</sub>BO<sub>3</sub> is expected. A shoulder on the low energy side of the primary peak was present on both the pre- and post-oxidized samples. It is possible that this shoulder was due to hydrated or hydroxide species. Again, no boron or B<sub>4</sub>C was detected.

## 2.4.2 Mechanical Properties

### 2.4.2.1 In-Plane (Warp) Tension

Tensile tests, with dog bone shaped samples 6.5" long by 0.75" wide, were performed based on ASTM D638 standard. Sample strains were monitored by the strain gauges attached to both surfaces of the specimens.

Tests were performed on both the as-cured and densified samples. The T-300 fabrics in the baselines differ from the inhibited samples in fiber batch and heat treatment lots. The as-cured tensile tests were conducted to check the variation in reinforcements. As shown in Table 8, the as-cured baseline composite tensile strength is ~ 17% greater than that of inhibited samples. No significant difference in tensile modulus was observed.

The tensile strength of the inhibited carbon-carbon composites was determined to be 39 Ksi. Although sufficient for most applications, this composite strength was about 30% lower than the 1427°C (2600°F) heat treated baseline composites which had a similar porosity content. Difference in the fiber strength, as determined from the as-cured composite, can not completely explain this 30% difference in composite strength. Fiber degradation in the inhibited composite, due to carborane addition, was the likely source of this loss of composite strength.

**Table 8**  
**Summary of Tensile Properties of Carbon-Carbon Composites**

Material	Process	Measured Properties		Fiber Volume V <sub>f</sub>	Corrected to 60% V <sub>f</sub>	
		Strength (Ksi)	Modulus (Msi)		Strength (Ksi)	Modulus (Msi)
Baseline	Cured	47.8	20.2	52.9%	54	22.9
Inhibited	Cured	41.4	19.5	53.8%	46	21.6
Baseline	2600°F HT	51.1	18.4	55%	56	20
Baseline	4 Densifications	55.5	18.0	55%	60	20
Inhibited	4 Densifications	39.8	17.3	61%	39	17

#### 2.4.2.2 Interlaminar Shear

Figure 26 shows the specimen configuration and loading fixture for the interlaminar shear test. The loading fixture was modified from Southern Research Institute's double-notch-shear fixture. A compression load was applied to the specimens for shear failure to occur between the two notches.

The interlaminar shear strength of carbon-carbon composites is strongly depended on the porosity content. As shown in Figure 27, the baseline material shows a significant improvement in shear strength as the porosity of the composite reduced to below 2% (with four densification). The interlaminar shear strength of the inhibited carbon-carbon composites is comparable to the baseline system with similar porosity content.

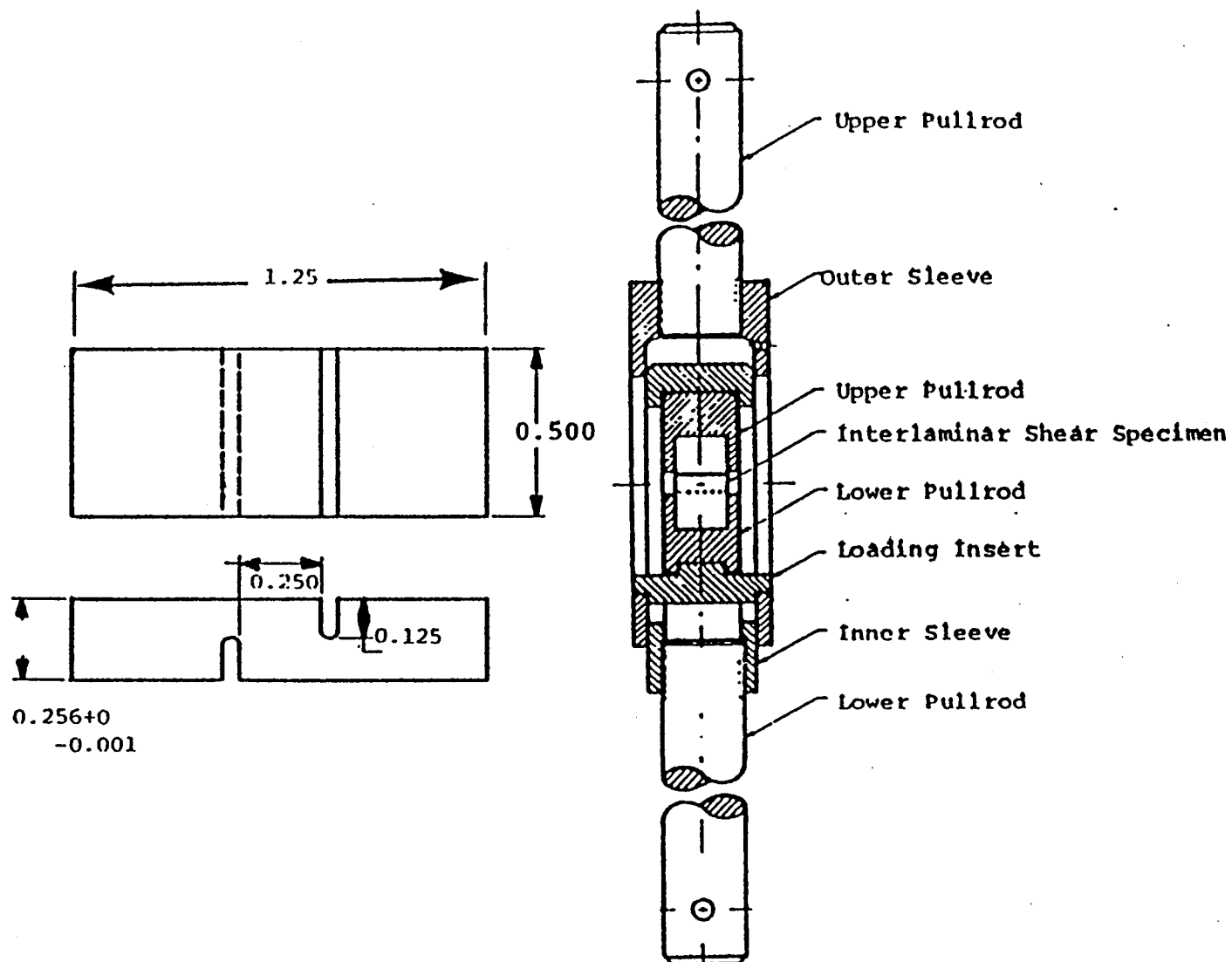
#### 2.4.3 Thermal Expansion

The thermal expansion of the carbon-carbon composites was measured from 30°C to 600°C in helium per ASTM test method D3386 using a thermomechanical analyzer (TMA). A 20 mN load was placed on the test specimen of 0.25"x0.25"x0.25" while it was heated under a ramp rate of 5°C/min. Changes in the height of specimens were measured and used for the calculation of the coefficient of thermal expansion (CTE).

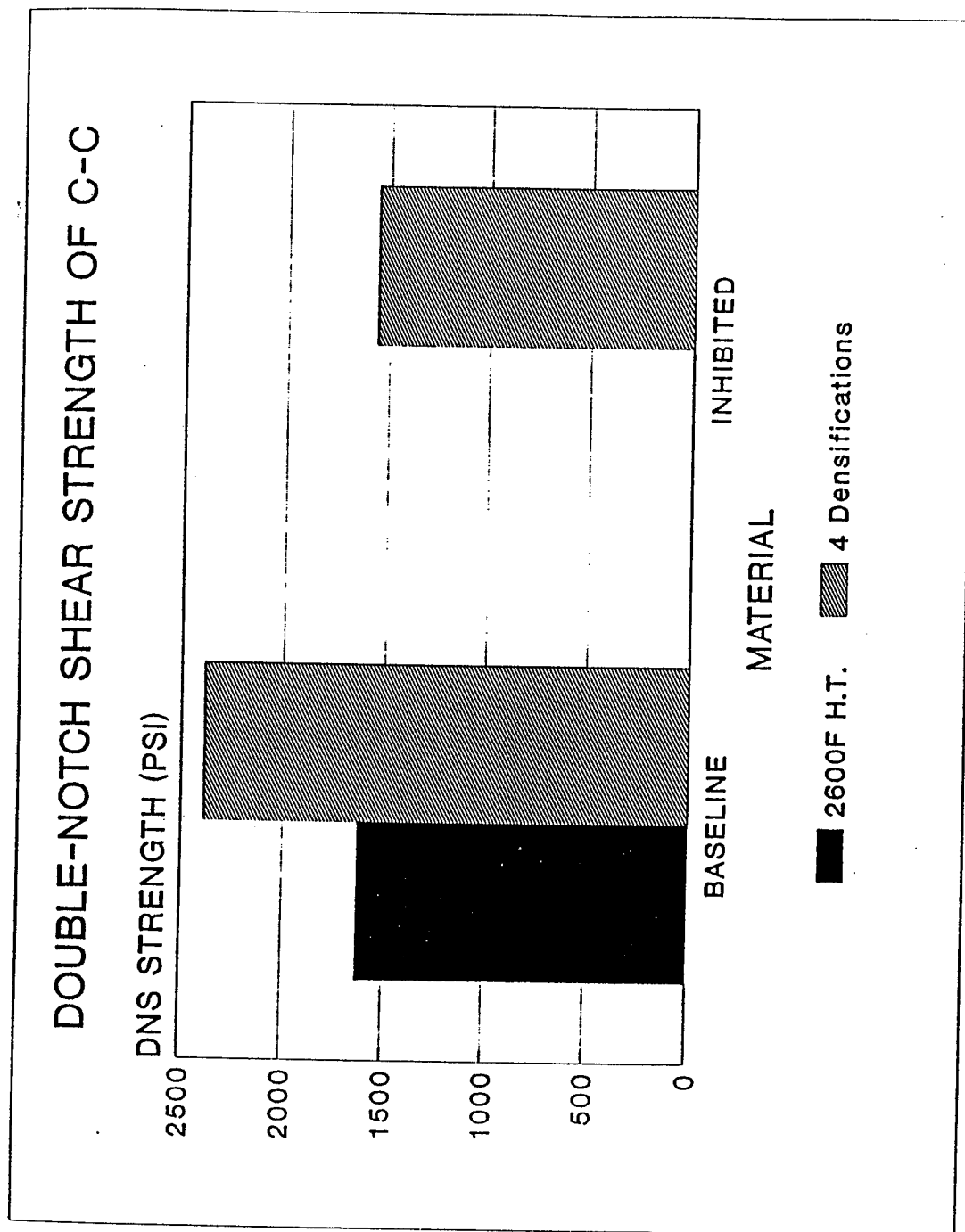
As shown in Table 9, the CTE in the warp direction is very small,  $\sim 1 \times 10^{-6}$  in/in°C, for both types of composite. These low CTE values suggest the dimensional stability along the fiber directions. The cross ply CTE's of the baseline and inhibited composite were determined to be 5.5 and  $7.1 \times 10^{-6}$  in/in°C, respectively. The increase in cross ply CTE of the inhibited composite can be attributed to the effect of boron oxide in the matrix.

**Table 9**  
**Summary of the CTE of Carbon-Carbon Composites**

Material	CTE (in/in°C)	
	Warp	Across Ply
Baseline Carbon-Carbon	$-1.0 \times 10^{-6}$	$5.5 \times 10^{-6}$
Inhibited Carbon-Carbon	$-0.9 \times 10^{-6}$	$7.1 \times 10^{-6}$



**Figure 26. Specimen Configuration and Loading Fixture for the Interlaminar Shear Test**



**Figure 27. Double Notch Shear Strength of Carbon-Carbon Composites**

#### 2.4.4 Oxidation Resistance

Both the baseline and inhibited carbon-carbon composites were tested under static conditions at 900°C and dynamically in a high heating rate muffle furnace with an air stream flowing at 8 SCFH. The dynamic test cycle was modified from the McAir oxidation cycle. There are five screening cycles prior to the modified McAir cycle (KA cycle) to determine the material stability and thermal shock resistance at each temperature used in the McAir cycle. Figure 28 shows the test cycles for both screening and McAir.

The inhibited carbon-carbon composites were also coated with SiC to improve their oxidation resistance. The SiC protective coating was provided by Chromalloy which consists of a 1-2 mil of RT43 and 8-10 mils of RT42. The RT42 coating was achieved by 6 CVD coating processes. During each coating process, the coating thickness for each sample was monitored by their weight gain. After each deposition, sample positions in the deposition chamber were rotated to even out the coating thickness between each sample.

##### 2.4.4.1 Static Test

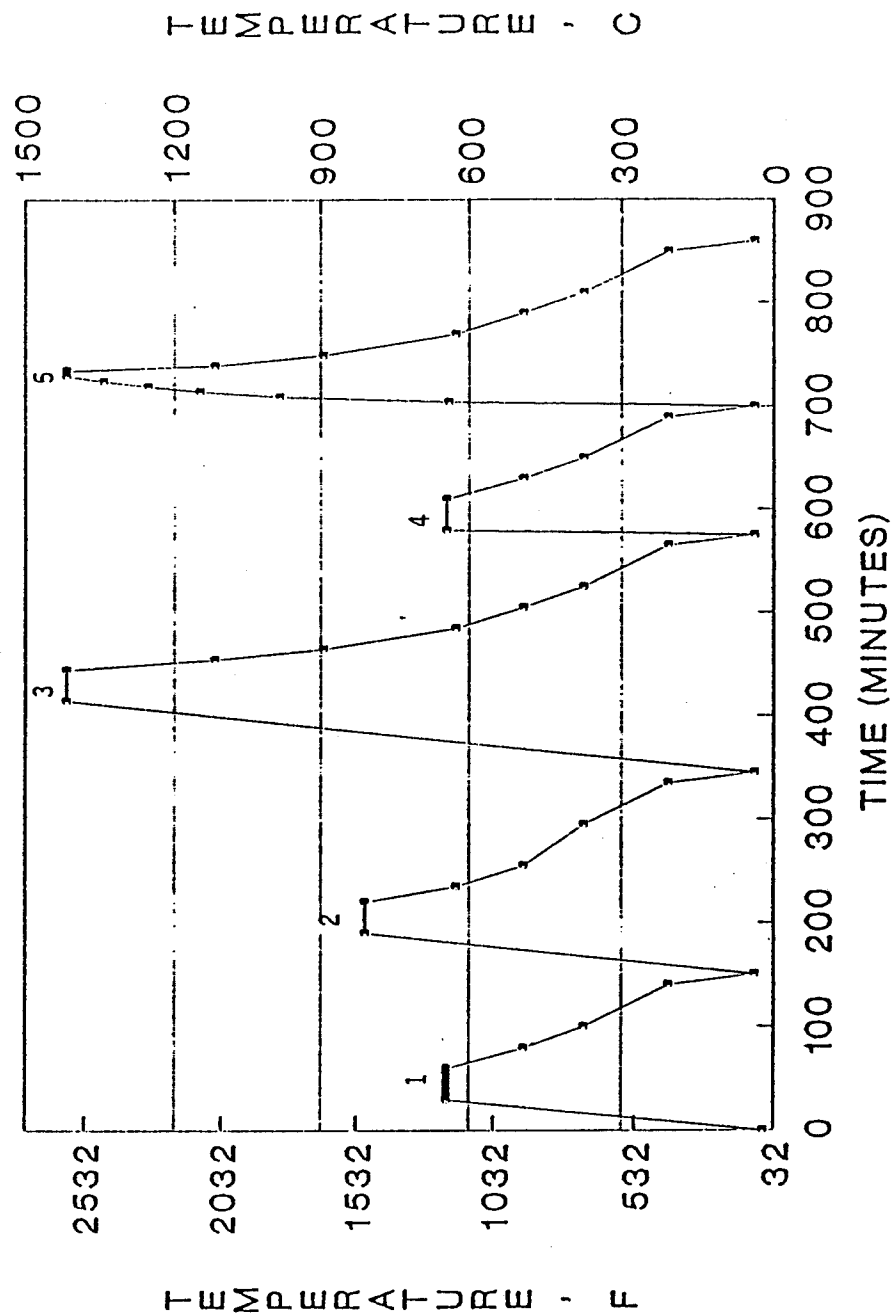
Static air oxidation tests at 900°C were performed on the RT42 coated inhibited composites, and uncoated (baseline and inhibited) samples. The weight loss results on the uncoated samples are questionable since the reinforcement fiber oxidizes at this high temperature. However, the inhibited sample did show slightly lower (~10%) weight loss than the baseline material.

The SiC coating of the coated samples cracked when it was cooled from the deposition temperature (~1100°C). Although the coated specimens were tested below their coating temperature, the coating cracks of the specimen induced by the residual tensile stress during cooling were believed to be mostly resealed. With this resealed SiC coating, combined with the sealant from matrix inhibitors, the SiC coated inhibited samples showed excellent oxidation resistance. No appreciable weight loss was observed after 300 hours at 900°C. Figure 29 shows the test results. An initial weight loss, approximately 1%, was observed in the initial stage of the test. This initial weight loss was believed to be outgasing from surface moisture as a similar ~1% weight loss was also observed from the TGA oxidation test at temperature below 200°C.

##### 2.4.4.2 Dynamic Test

Figure 30 shows the results of oxidation screening tests at 649°C (1200°F) and 816°C (1500°F) on uncoated samples. As expected, the baseline materials suffered severe oxidation. Surprisingly, the inhibited matrix did not significantly improve the oxidation resistance of the composite. Visual examination of the oxidized samples indicated severe matrix oxidation. Highly oxidized samples were readily delaminated due to the loss of matrix.

# KA OXIDATION CYCLE ( SCREENING )



\* The Heating and Cooling Sections of Test Cycle 3 were Accomplished in Flowing Nitrogen While the Rest of the Test Cycles was Accomplished in Flowing Air

Figure 28(a). Test Cycle for Screening

# KA CYCLE ( AIR OXIDATION )

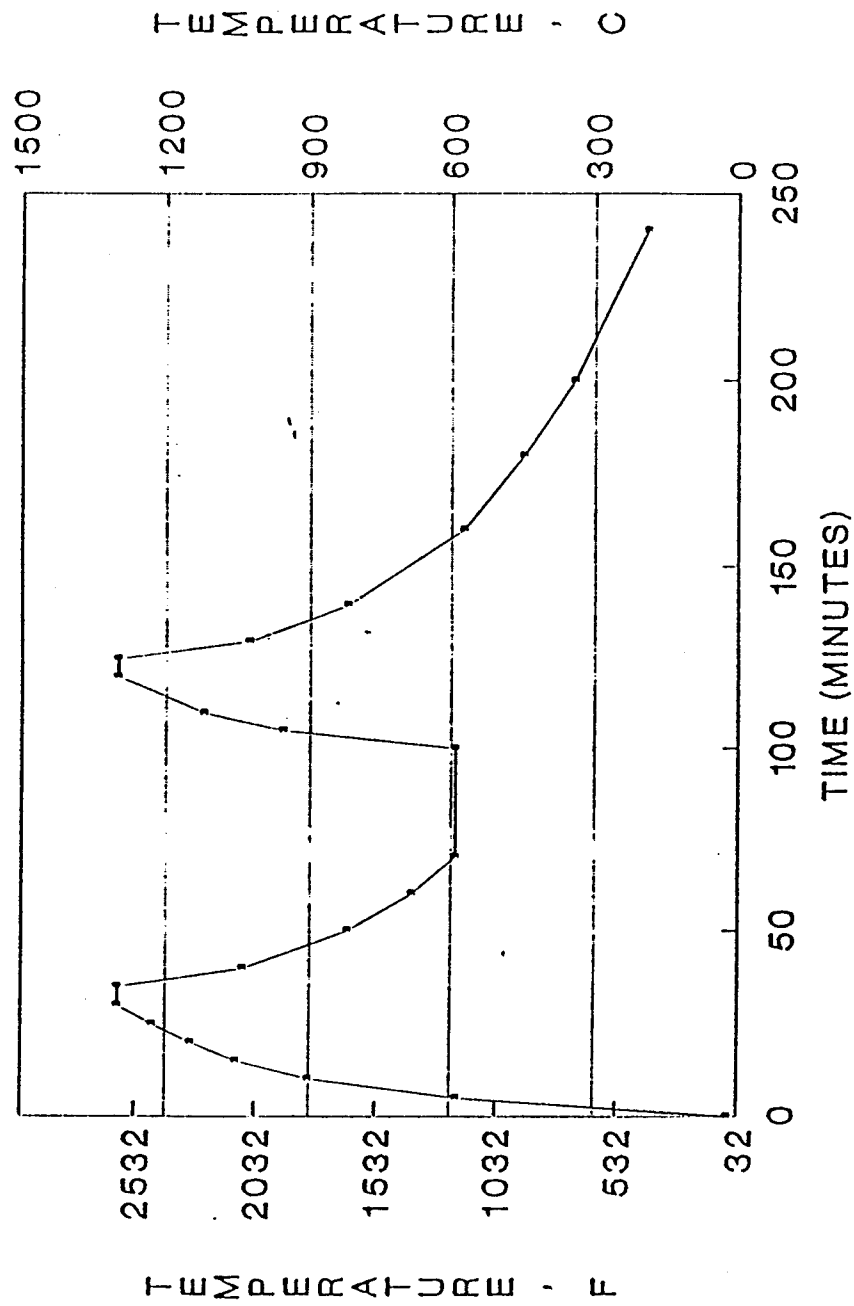


Figure 28(b). Test Cycle for McAir



# STATIC OXIDATION OF INHIBITED C-C - at 900 degree C

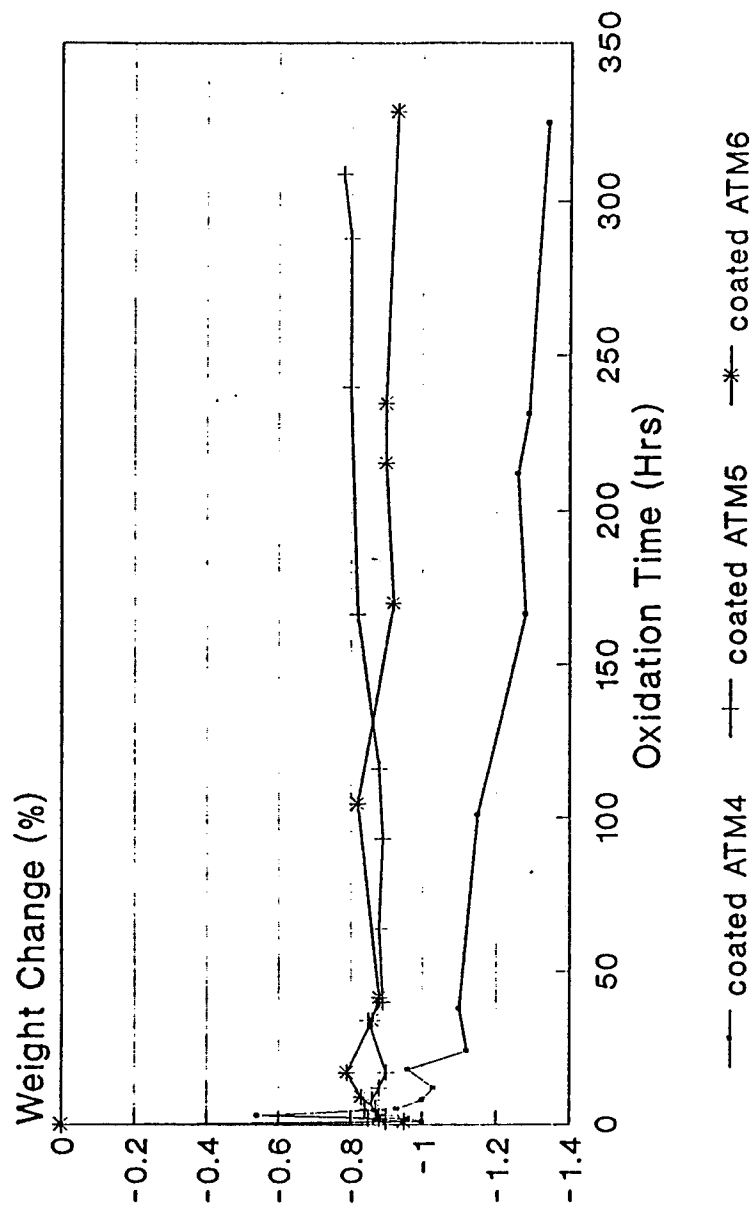
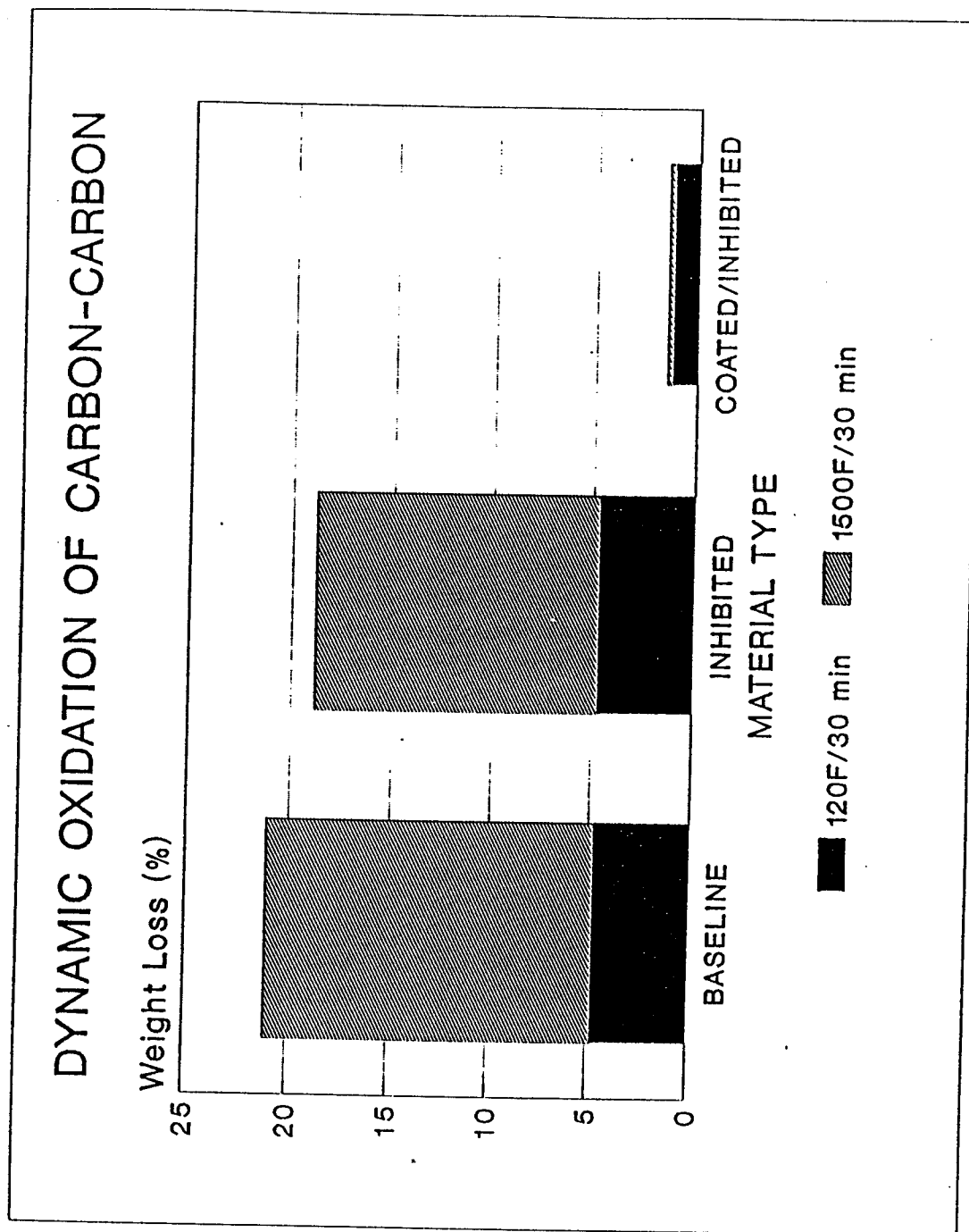


Figure 29. Static Oxidation Test Results of Carbon-Carbon Composites, 900°C



**Figure 30. Dynamic Oxidation Test Results of Inhibited Carbon-Carbon, 1200°F and 1500°F Screening**

Examination of the dynamically oxidized specimens, through SEM, revealed small nodules on the inhibited specimens. (Figure 31) A thin and uniform coating was also observed visually on the surface ply of the inhibited samples. The nodules present over the oxidized specimens and the uniform coatings over the surface plies were suspected to be boron oxide from the oxidation of carborane in carbon chars. A few nodules were also observed on the surface of the baseline specimens. (Figure 32) It is suspected that boron or boron compounds were transferred from the inhibited system to the surface of the baseline composites during the 1427°C heat treatment.

Oxidation of inhibited matrix can be attributed to several factors. First, the composites may not have sufficient boron to prevent oxidation as they were heat treated to 1427°C.  $B_2O_3$  may evaporate at this high temperature due to its high vapor pressure. Secondly, oxidation resistance of the boron doped carbon matrix may be affected by the air flow used for the oxidation tests as the previous results were based on static tests. Finally, the size of the carbon char may also affect their oxidation resistance as these are very small in the carbon-carbon composite. To better understand the oxidation behavior of the inhibited chars, several simple experiments were performed.

Cured phenolic (SC1008) and Code88A liquid pitches were carbonized separately at 816°C (1500°F) and 1427°C (2600°F). The carbonized chars were sent out for boron content, and oxidized under various conditions. Table 10 lists the test results. The 1427°C heat treatment did not reduce the boron content in carbon chars through evaporation of  $B_2O_3$ . On the contrary, it improved significantly the oxidation resistance of carbon char. Amount of air flow and sample size used for oxidation test did affect the oxidation resistance of carbon char. Samples with size less than 200mg oxidized significantly.

Boron doping of composite matrix could not prevent oxidation due to the small size of carbon char that are limited by the composite ply thickness. The oxidation resistance of the carbon char may be improved with higher concentration of boron doping. However, even doubling of the boron content, coupled with the addition of calcium, did not compensate for the small particle size of the carbon char by completely inhibit the oxidation of the char.

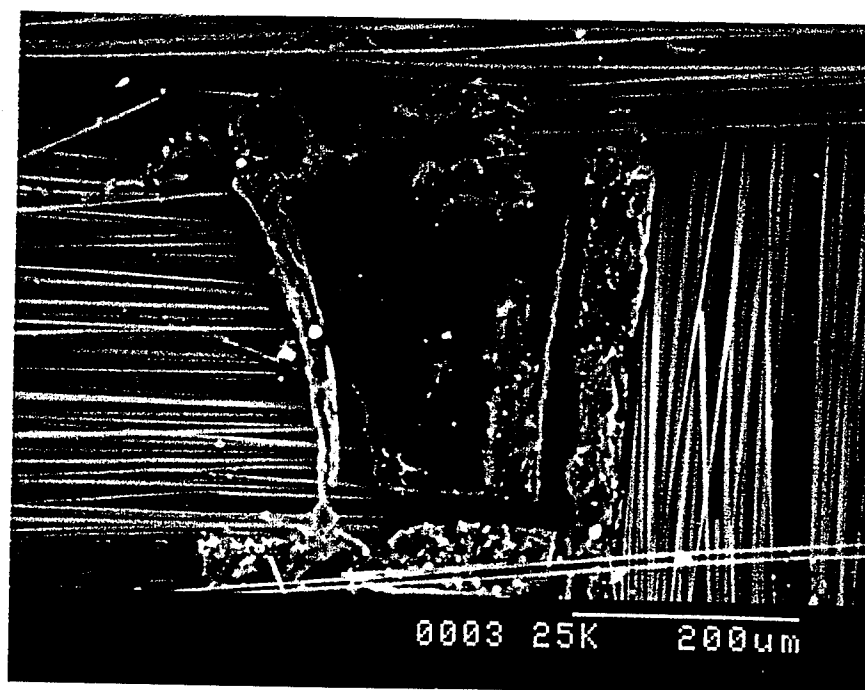
Figure 30 also shows the screening test results on SiC coated inhibited composites. As expected, SiC coating reduced the oxidation of the carbon-carbon composites. Coated samples suffered more oxidation at 649°C (1200°F) than 816°C (1500°F) due to the wider opening of coating cracks at 649°C.

#### 2.4.4.3 Kaiser Cycle

Figure 33 shows the oxidation results of the SiC coated inhibited composite coupons. A weight loss of ~ 2% was detected in the initial screenings at 649, 816 and 1427°C. The surface coating buckled after the 1427°C screening due to residual compressive stress. The damaged coating failed to provide adequate oxidation protection on the carbon-carbon substrate, resulting in the rapid weight loss shown for the SiC coated inhibited composites.



**Figure 31. SEM Photomicrograph of the Oxidized Inhibited Composite**



**Figure 32. SEM Photomicrograph of the Oxidized Baseline Composite**

# OXIDATION OF INHIBITED CARBON-CARBON

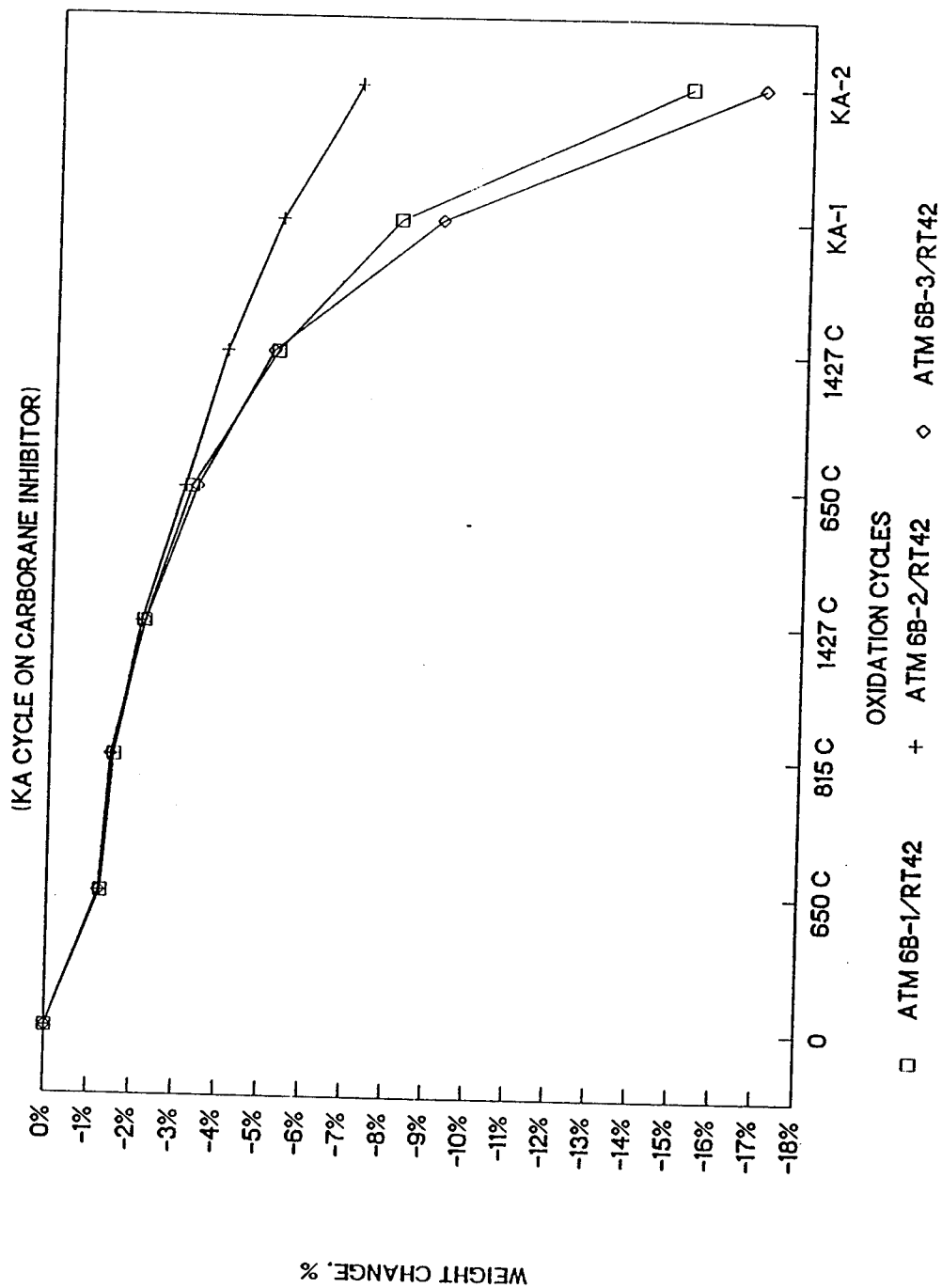


Figure 33. Oxidation Test results of SiC Coated Inhibited Carbon-Carbons

**Table 10 Oxidation Resistance of Carbon Chars  
900°C, 1 Hour**

<u>Sample I.D.</u>	<u>%B</u>	<u>Sample Wt. (mg)</u>	<u>Air Flow (ccm)</u>	<u>% W.L.</u>
SC1008, 816°C	5.8	270	100	10.1
		60	500	57.0
SC1008, 1427°C	5.9	180	100	1.1
		60	500	18.0
Code88A, 816°C	4.1	178	100	6.0
		48	500	30.0
		248	500	8.0
Code88A, 1427°C	3.7	323	100	1.6
		93	500	9.0
		159	500	6.5
SC1008, 900°C with 1.42% Ca	9.2	81	100	23.0

### 3. Conclusions

Molecular sources of boron and calcium were used to improve the oxidation and moisture resistances of carbonaceous materials. Carborane, a robust chemical, was chosen as the precursor for atomically dispersed boron. Carborane additions improved the oxidation resistance of carbon chars significantly. Unfortunately, carborane modified carbon chars suffer the common problem of moisture affinity associated with boron. It was also observed that up to 40% of the added carborane, an expensive chemical, was sublimed during the carbonization process. To overcome the problems of moisture sensitivity and carborane loss, molecular dispersion of calcium and direct attachment of carborane to furfuryl molecule were evaluated.

Calcium methoxyethoxide and calcium isopropoxide were identified as precursors for molecular dispersion of calcium. Calcium isopropoxide and calcium methoxyethoxide have limited solubility in phenolic or furfuryl resins. Although the solubility of these compounds in phenolic resin can be improved through addition of a third solvent, such as methoxyethanol for calcium methoxyethoxide, introduction of the third solvent complicated the manufacturing process. Moisture sensitivity of the calcium compound prevented it from curing in air, and residual solvent caused foaming problems during the carbonization process.

Since no calcium organometallic compounds studied were promising in providing calcium for moisture resistance, no calcium was added in the carborane modified SC1008 phenolic resin during the preparation of prepregs. The Code88A liquid pitch

that was chosen as the impregnant for composite densifications did not suffer moisture attack.

Improvement of carborane retention, through synthesis of furylcarborane, proved to be very difficult. The coupling product formation in the case of *o*-carboranes/2-substituted furans is extremely sensitive to the electronic effect of the substituents, in sharp contrast to well-known aromatic/heteroaromatic reactions. No coupling product was found for 1-methyl-*o*-carborane and 1-tert-butyldimethylsilyl-*o*-carborane reactions. 2-tert-Butyldimethylsiloxyethyl furan derivatives appeared to be inactive for coupling with carboranes. Only unsubstituted *o*-carboranyl copper reactions with 2-iodofuran or 5-bromofuroic acid methyl ester produced some amount of furylcarborane derivatives which are the major products in the initial stages of reaction. However, both coupling products: 1-furyl-*o*-carborane and 5-(1-*o*-carboranyl)-2-furoic acid methyl ester are sensitive to polymerization. This led to a substantial transformation of reactants into tars in the reaction mixture and/or during the usual work up and purification procedures, making the yield of desired product far less than satisfactory.

Carborane modified carbon-carbon composites were successfully fabricated using standard processes with minor adjustments. The onset of exothermic reaction in the carborane inhibited prepreg, detected by DSC, started at a lower temperature than the standard material. The composite surface tended to cure prematurely when processed in a slow heating autoclave. A hot press was used to prevent the delamination of composite panels due to premature curing of composite skin.

In a standard carbon-carbon fabrication process samples were graphitized at 2482°C, after the first carbonization, to open up the porosity. To prevent the evaporation of boron oxide, which has a boiling point of 1860°C, carborane modified composite samples were not graphitized. Without this critical porosity-opening graphitization process, the efficiency of densification and the density of the composite were compromised. An extra densification process was needed to achieve a comparable density and open porosity to the standard composites.

The tensile strength of the carborane modified carbon-carbon composite was about 15% less than the as-cured composite strength. For comparison, a standard carbon-carbon composite with similar density has a tensile strength slightly greater than its as-cured strength. This strength reduction is attributed to the fiber degradation during composite processing. Although the tensile strength of the carborane modified carborane-carbon composite was compromised, but it should be sufficient for most applications. Also, the interlaminar strength of the composite was not affected by the addition of carborane.

The oxidation resistance of the inhibited carbon-carbon composites was determined. Carborane inhibition improved the oxidation resistance of the carbon-carbon composite, but failed to protect the composite completely. The oxidation resistance of the carborane added carbon char was strongly dependent on the sample size. Due to the size limitation of carbon char, an inhibited composite with SiC protective coating suffered significant oxidation at 649°C. At 1427°C, compressive residual stress

induced buckling of the SiC coating. The damaged coating failed to provide the oxidation protection for carbon-carbon substrate.

#### 4. Suggestions for Future Work

Direct reaction of calcium metal with phenolic resin can be used for the incorporation of calcium molecule into phenolic resin. This calcium modified phenolic resin can be cured in air and carbonized without foaming problem. Complete retention of boron can also be achieved using this precursor.<sup>13</sup>

Theoretically, about 30 mole % of CaO is required to completely protect the B<sub>2</sub>O<sub>3</sub> glass. This corresponds to a ~5 wt% calcium addition to the resin. To enhance the efficiency of calcium incorporation, a fine calcium powder can be added to the phenolic resin to increase the reaction rate. The surface area of calcium can be significantly increased with particle size reduction. Ammonia can also be used as a catalyst to expedite the reaction between calcium and the phenolic resin.

Oxidation resistance of the boron doped carbon char depends strongly on the size of the sample. Small sample size suffers significant oxidation due to large surface area. Improvement in oxidation resistance was observed on carbon char with increasing boron content. A much higher concentration of boron doping may be needed for the protection of small size carbon char. The effect of boron concentration on the oxidation resistance of small carbon char needs to be determined.

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## **Phase II Statement of Work**

The contractor developed the fabrication process of oxidation resistant carbon-carbon composite through atomic dispersion strategy. This work was directed at improving the oxidation and moisture resistance of the inhibited carbon-carbon composites.

The work performed consisted of the following tasks:

1. Determine the carborane retention rate in phenolic, furfuryl and pitch (Code88) systems.

A fixed amount of carborane will be added into the resin systems separately. After the cure and carbonization processes, the percentage boron retention of these systems will be determined by EDS analysis. The best system will be chosen for composite densifications.

2. Identify the calcium precursors for moisture protection.

Various high calcium content organometallic compounds, such as calcium-isopropoxide and calcium methoxyethoxide, will be added into the boron modified resin systems. The solubilities of the compounds in the resins and the calcium retention rates after the carbonization will be determined. The most promising precursor will be used to densify the carbon-carbon composites.

3. Develop the prepregging process using the modified resin system.

Boron and calcium modified phenolic resin will be used to prepare the prepregs for the composite fabrication. Quality control processes, such as % resin content, % flow and % volatile, of the modified phenolic resin systems will be developed

4. Develop the composite fabrication process using the modified resin systems.

The composite fabrication processes: cure, carbonization, graphitization, and densification, using the modified resin system will be developed. Panels will be fabricated for physical and oxidation properties characterization.

5. Characterize the physical and mechanical properties of the oxidation inhibited carbon-carbon composites.

The tensile (in-plane) strength, interlaminar shear strength and thermal expansion of the boron/calcium modified carbon-carbon composites will be determined. Properties of the unmodified composites will also be determined for comparison.

6. Evaluate the oxidation resistance of the protected carbon-carbon composites.

TGA oxidation tests are planned for the modified and unmodified samples. The modified samples will also be coated with SiC and tested statically in air. The most promising samples will be tested under cycling conditions.

7. Characterize the compositional state of the boron and calcium.

Auger electron spectroscopy and X-ray photoelectron spectroscopy will be used to characterize the boron and calcium states of the modified composites. Both the oxidized and unoxidized samples will be examined.

8. Fabrication of a prototype carbon-carbon composite component for strength and oxidation testings.

A prototype carbon-carbon composite component agreeable to AFOSR and Kaiser will be fabricated for application test.

9. Prepare interim and final reports describing the experiments and results

Annual interim and final reports describing the details of the experiments and results will be submitted.

### **Publications in Technical Journals**

Publications are planned for the Carbon Conference.

### **Professional Personnel**

#### Philip S. Chen, Principle Investigator

Ph.D. in Materials Engineering, Rensselaer Polytechnic Institute, 1982.  
M.S. in Materials Engineering, Rensselaer Polytechnic Institute, 1979.

Dr. Chen is Director of Aerospace Research and as such is responsible for a number of coated fiber and CVD programs at ATM. Dr. Chen has broad experience in the research and development of materials for aerospace applications, particularly in the area of high temperature materials. Formerly with Kaiser Aerotech, he has particular experience in carbon-carbon and ceramic matrix composites

#### Ward C. Stevens, Program Manager

Ph.D. in Materials Science, Rensselaer Polytechnic Institute, 1985

Dr. Stevens is Vice President and chief operational office of ATM's thin film coatings business. Dr. Stevens has developed a number of coated fiber products for ATM and holds nine patents related to fiber coating. Prior to joining ATM, Dr. Stevens developed a process for coating carbon fibers with copper and the subsequent consolidation of these fibers into metal matrix composites. He has also conducted

research in coating fibers by plasma-assisted CVD, chemical vapor infiltration of carbon fiber tow and the development of carbon fibers from petroleum pitch.

H. O. Davis, Kaiser Aerotech

MBA, Texas Christian University, 1962

Mr. H.O.Davis, Vice President and Director of Kaiser R&D, is program manager for the subcontract part of the work. Mr Davis is responsible for all research and development at Kaiser Aerotech and has over twenty years experience with rocket materials.

Maitland Jones, Jr., Princeton University

Ph. D., Yale University, New Haven, Connecticut, 1963

Professor Jones is David B. Jones Professor of Chemistry, Princeton University, and a well-known expert in carborane chemistry. Professor Jones is widely known as an authority in the generation and chemistry of reactive intermediates. He discovered the relationship between the spin state of a carbene and the stereochemistry of its reaction with an olefin. In recent years, he has concentrated on the synthesis and generation of molecules that test the fundamental concepts of chemical bonding and molecular rearrangements.

Igor R. Likhotvorik, Princeton University

Ph. D. in Chemistry, Kiev Polytechnic Institute, 1982.

Dr. Likhotvorik is a Postdoc. Research Fellow at Chemistry Department, Princeton University. Dr. Likhotvorik worked on the synthesis of carborane-phenol monomer. A native of Ukraine, Dr. Likhotvorik is also Associate Professor of Chemistry, Kiev Polytechnic Institute.

**Interactions**

None.

**Patent Disclosures**

None.

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